

EXHIBIT D

ANALYTICAL METHODS

EXHIBIT D - ANALYTICAL METHODS

Table of Contents

<u>Section</u>	<u>Page</u>
I INTRODUCTION	D-3
II SAMPLE PRESERVATION AND HOLDING TIMES	D-7
PART A - Sample Preservation	D-7
PART B - Contract Required Holding Times	D-8
III SAMPLE PREPARATION	D-9
Part A - Medium Level Digestion Procedure for Aqueous Samples (Medium and Low Level)	D-10
Part B - Low Level Digestion Procedure for Aqueous Samples (Low Level)	D-12
Part C - Soil/Sediment/Solid Sample Digestion Procedure	D-18
Part D - Microwave Digestion Procedure for Aqueous (Medium and Low Level) and Soil/Sediment/Solid Samples	D-21
Part E - Mercury Sample Preparation	D-27
Part F - Cyanide Sample Preparation	D-27
Part G - Total Organic Carbon Sample Preparation	D-27
Part H - Total Combustible Organics Sample Preparation	D-27
Part I - Grain Size Distribution Sample Preparation	D-27
IV SAMPLE ANALYSIS	D-28
Part A - Inductively Coupled Plasma-Atomic Emission Spectrophotometric Method	D-29
Part B - Atomic Absorption Methods, Furnace Technique	D-39
Part C - Atomic Absorption Methods, Flame Technique	D-54
Part D - Cold Vapor Methods for Mercury Analysis	D-59
Part E - Methods for Total Cyanide Analysis	D-72
Part F - Percent Solids Determination Procedure	D-91
Part G - Total Organic Carbon in Aqueous and Soil/Sediment Samples	D-93
Part H - Total Combustible Organics in Soil/Sediment Samples	D-120
Part I - Grain Size Distribution in Soil/Sediment Samples	D-128

SECTION I
INTRODUCTION

1.0 General Analytical Scheme

Exhibit D contains procedures for sample preparation and analysis of the target analytes. Listed below is a summary of the sample preparation and analysis procedures contained in this SOW and the applicable sections:

- 1) Target analyte metals for analysis by ICP (Section IV, Part A), furnace AA (Section IV, Part B), and/or flame AA (Section IV, Part C):
 - Medium Level aqueous samples - Medium Level digestion procedure (Section III, Part A or D);
 - Low Level aqueous samples - Medium Level digestion procedure (Section III, Part A or D); or Low Level digestion procedure only if, using the most sensitive instrumental technique in Exhibit D, preconcentration is required to meet Low Level CRQL requirements of Exhibit C (Section III, Part B);
 - Soil/Sediment/Solid samples - (Section III, Part C or D);
- 2) Mercury in aqueous (Medium and Low) and soil/sediment/solid samples (Section IV, Part D);
- 3) Cyanide in aqueous (Medium and Low) and soil/sediment/solid samples (Section IV, Part E);
- 4) Percent solids determination for target analyte metals and cyanide (Section IV, Part F);
- 5) Total organic carbon in aqueous and soil/sediment samples (Section IV, Part G);
- 6) Total combustible organics in soil/sediment samples (Section IV, Part H); and
- 7) Grain size distribution in soil/sediment samples (Section IV, Part I).

The target analyte list may be designated as all target analytes listed in Exhibit C, or a subset of those analytes, and will be indicated on the chain of custody accompanying each Sample Delivery Group (SDG).

1.1 Permitted Methods

Any of the analytical methods specified in Exhibit D may be used as long as the documented method detection limits achieve the Contract Required Quantitation Limit requirements in Exhibit C. Analytical methods with higher method detection limits may be used only if the sample concentration exceeds five times the documented detection limit of the method.

1.2 Initial Run Undiluted

All samples must initially be run undiluted (i.e., final product of the sample preparation procedure). When an analyte concentration exceeds the calibrated or linear range (as appropriate), reanalysis for that analyte(s) is required after appropriate dilution. The Contractor shall use the least dilution necessary to bring the analyte(s) within the valid analytical range (but not below the CRQL) and report the highest valid value for each analyte as measured from the undiluted and diluted analyses. Unless the Contractor can submit proof (i.e., raw data) that dilution was required to obtain valid results, both diluted and undiluted sample measurements must be contained in the raw data. ICP data showing a high concentration for a particular analyte, combined with an analyte result that is close to the middle range of the calibration curve in the diluted sample, constitute sufficient proof that the sample had to initially be run diluted for that analyte on a furnace AA instrument. All sample dilutions shall be made with

deionized water appropriately acidified to maintain constant acid strength.

1.3 Quality Assurance/Quality Control Measurements

The Contractor is reminded and cautioned that Exhibit D is a compendium of required and/or permitted analytical methods to be used in the performance of analyses under this contract. The quality assurance/quality control procedures or measurements to be performed in association with these methods or analyses are specified in Exhibit E. In the event references to quality assurance measurements in any of the methods appear to be in conflict with or to be less stringent than the requirements of Exhibit E, the requirements of Exhibit E will prevail.

1.4 Raw Data Requirements

The Contractor is reminded and cautioned that the collection and provision of raw data may or may not be referred to within the individual methods of Exhibit D or the Quality Assurance Protocol of Exhibit E. The Raw Data Deliverables requirements are specified in Exhibit B, Section II. Raw data collected and provided in association with the performance of analyses under this contract shall conform to the appropriate provisions of Exhibit B.

1.5 Glassware Cleaning

Lab glassware to be used in metals analysis must be acid cleaned according to EPA's manual "Methods for Chemical Analysis of Water and Wastes" or an equivalent procedure.

1.6 Standard Stock Solutions

Stock solutions to be used for preparing instrument or method calibration standards may be purchased or prepared as described in the individual methods of Exhibit D. All other solutions to be used for quality assurance/quality control measurements shall conform to the specific requirements of Exhibit E.

1.7 Aqueous Sample pH Measurement

Before sample preparation is initiated on an aqueous sample received in shipment, the Contractor shall check the pH of the sample and note in a preparation log if the pH is <2 for a metals or TOC sample, or if the pH is >12 for a cyanide sample. The Contractor shall not perform any pH adjustment action if the sample has not been properly preserved. If the sample has not been properly preserved, contact the RSCC, before proceeding with the preparation and analysis, to inform EPA of the situation. For all samples not properly preserved, the Contractor shall note the problem, the EPA sample numbers for the affected samples and any instructions given by the Region in the SDG Narrative.

1.8 Sample Mixing

Unless instructed otherwise by the EPA, all samples shall be mixed thoroughly prior to aliquoting for digestion. No specific procedure is provided herein for homogenization of soil/sediment/solid samples; however, every effort should be made to obtain a representative aliquot.

1.9 Dissolved Metals

If dissolved metals analyses are requested by the EPA, the Contractor shall follow the instructions on the Traffic Report(s) regarding whether the samples shall be digested. If EPA indicates on the Traffic Report that a digestion is to be performed when analyzing field samples for dissolved metals, then the Contractor shall digest the samples using the procedures for total metals.

If the EPA indicates on the Traffic Report that a digestion is not to be performed when analyzing field samples for dissolved metals, then an aqueous laboratory control sample (LCS) and a post-digestion (hardcopy Form 5B) spike sample are not required.

1.10 Background Corrections

Background corrections are required for flame AA measurements below 350 nm and for all furnace AA measurements. For ICP background correction requirements, see Exhibit D Section IV, Part A.

1.11 Replicate Injections/Exposures

Each furnace analysis requires a minimum of two injections (burns), except for full method of standard additions (MSA). All ICP measurements shall require a minimum of two replicate exposures. Appropriate hard copy raw data for each exposure/injection shall be included in the data package in accordance with Exhibit B, Section II. The average of each set of exposures/injections shall be used for standardization, sample analysis, and reporting as specified in Exhibit D.

1.12 Insufficient Sample Amount

If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the RSCC to apprise them of the problem. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. All changes in the analyses **must** be preapproved by the Region I Project Officer. The Contractor shall document the Region's decision (including sample weight/volume prepared and analyzed) in the SDG Narrative.

1.13 Multiphase Samples

If multiphase samples (e.g., a two-phase liquid sample) are received by the Contractor, the Contractor shall contact the RSCC to apprise them of the type of sample received. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do one of the following:

Exhibit D -- Section I
Introduction

- Mix the sample and analyze an aliquot from the homogenized sample.
 - Separate the phases of the sample and analyze each phase separately. The RSCC will provide EPA sample numbers for the additional phases.
 - Separate the phases and analyze one or more of the phases, but not all of the phases. The RSCC will provide EPA sample numbers for the additional phases, if required.
 - Do not analyze the sample.
- 1.13.1 If all of the phases are not amenable to analysis (i.e., outside the scope of the SOW), then the Region may require the Contractor to do one of the following:
- Separate the phases and analyze the phases that are amenable to analysis. The RSCC will provide EPA sample numbers for the additional phases, if required.
 - Do not analyze the sample.
- No other change in the analyses will be permitted. The Contractor shall document the problem, the EPA sample numbers for the affected samples and the Region's instructions in the SDG Narrative.
- 1.14 Percent Solids for Soil/Sediment/Solid Samples
- Prior to sample preparation and analysis, the Contractor shall determine the sample's percent solids using the procedure in Section IV, Part F.
- 1.14.1 If the percent solids of the sample as determined above is greater than 30 percent ($> 30\%$), the Contractor shall proceed with preparation and analysis for soil/sediment/solid samples as described Exhibit D.
- 1.14.2 If the percent solids of the soil/sediment/solid sample is less than or equal to 30 percent ($\leq 30\%$), then the Contractor may be required to utilize a larger amount of sample or remove the majority of the water in accordance with Section IV, Part F. The Region may request that the samples not be analyzed or another method of analysis be used.
- 1.14.3 For all samples that do not meet the greater than 30 percent solids ($> 30\%$) requirement, the Contractor shall note the problem, the EPA sample numbers for the affected samples, the initial and subsequent percent solid(s), and the steps taken to achieve the dry weight CRQL requirements including the sample weight/volume prepared and analyzed, the final digestate volume, and the Region's instructions in the SDG Narrative.
- 1.15 ICP Analysis
- Whenever the ICP is utilized to analyze and report one or more target analytes, then aluminum, calcium, iron, magnesium, and all other analytes which were determined to be a spectral interference (as specified in Exhibit E, section 5.13) shall also be analyzed and reported with the samples in the SDG in accordance with the requirements of this contract.

SECTION II

SAMPLE PRESERVATION AND HOLDING TIMES

1.0 SAMPLE PRESERVATION

- 1.1 If samples are received in containers other than those specified in Table 1, Sample Preservation and Container Requirements, then the Contractor shall contact the RSCC to ascertain the proper procedure for subsampling from the sample container. If samples are received not properly preserved as specified in Table 1, then the Contractor shall contact the RSCC to ascertain whether or not the sample should be analyzed. For all samples that were not properly preserved, or not in the proper containers, the Contractor shall note the problem, the EPA sample numbers for the affected samples and fraction (e.g., cyanide), and the Regional instructions in the SDG Narrative.

Table 1 - Sample Preservation and Container Requirements

Measurement	Aqueous		Soil/Sediment/Solid	
	Preservative ⁽²⁾	Container ⁽¹⁾	Preservative ⁽²⁾	Container ⁽¹⁾
Metals	HNO ₃ , pH<2	P,G	Cool, maintain at 4°C(±2°C) until analysis	P,G
Mercury	HNO ₃ , pH<2	P,G	Cool, maintain at 4°C(±2°C) until analysis	P,G
Cyanide	0.6g ascorbic acid ⁽³⁾ ; NaOH to pH>12; Cool, maintain at 4°C(±2°C) until analysis	P,G	Cool, maintain at 4°C(±2°C) until analysis	P,G
Total Organic Carbon	H ₂ SO ₄ , pH<2, cool, maintain at 4°C(±2°C) until analysis	G	Cool, maintain at 4°C(±2°C) until analysis	G
Total Combustible Organics	---	---	Cool, maintain at 4°C(±2°C) until analysis	G
Grain Size Distribution	---	---	---	P,G

- FOOTNOTES:**
- (1) Polyethylene (P) or glass (G).
 - (2) Sample preservation is performed by the sampler immediately upon sample collection.
 - (3) Only used in the presence of residual chlorine.

Exhibit D -Section II
Sample Preservation and Holding Times

2.0 CONTRACT REQUIRED HOLDING TIMES

- 2.1 Analysis of water and soil/sediment/solid samples must be completed within the contract required holding times specified in Table 2, Contract Required Holding Times. Holding times are from the Validated Time of Sample Receipt (VTSR).

Table 2 - Contract Required Holding Times

Measurement	Holding Times ⁽¹⁾	
	Water	Soil/Sediment/Solid
Metals	180 days	180 days
Mercury	26 days	26 days
Cyanide	12 days	12 days
Total Organic Carbon	26 days	12 days
Total Combustible Organics	---	12 days
Grain Size	---	180 days

FOOTNOTES:

- (1) Holding times are from Validated Time of Sample Receipt.
- 2.2 As part of the Agency's QA program, the Agency may provide Performance Evaluation (PE) samples which the Contractor is required to prepare per the instructions provided by the Agency. The PE samples must be analyzed and reported with the samples with which they were received.
- 2.3 If samples submitted for analysis have exceeded holding times and have not yet been analyzed, then the Contractor shall contact the RSCC to ascertain whether or not the samples should be analyzed. Note that this notification requirement in no way obviates the contractual requirement for the Contractor to analyze samples within holding times. If the Contractor is instructed to proceed with analysis outside holding times, sample price may be reduced depending upon the impact of the noncompliance on data usability. For all samples that exceeded holding times, the Contractor shall note the problem, the EPA sample numbers for the affected samples, and the Regional instructions in the SDG narrative.
- 2.4 Data reported from sample analyses which were performed outside the contract required holding times for the requested analysis shall be subject to a commensurate reduction in sample price or zero payment due to data rejection depending upon the impact of the noncompliance on data usability.

SECTION III

SAMPLE PREPARATION

	<u>Page No.</u>
Part A - Medium Level Digestion Procedure for Aqueous Samples (Medium and Low Level)	D-10
Part B - Low Level Digestion Procedure for Aqueous Samples (Low Level)	D-12
Part C - Soil/Sediment Sample Digestion Procedure	D-18
Part D - Microwave Digestion Procedure for Aqueous (Medium and Low Level) and Soil/Sediment Samples	D-21
Part E - Mercury Sample Preparation	D-27
Part F - Cyanide Sample Preparation	D-27
Part G - Total Organic Carbon Sample Preparation	D-27
Part H - Total Combustible Organics Sample Preparation	D-27
Part I - Grain Size Distribution Sample Preparation	D-27

**PART A - MEDIUM LEVEL DIGESTION PROCEDURE FOR AQUEOUS SAMPLES
(MEDIUM AND LOW LEVEL)**

Acid Digestion Procedure for ICP, Flame AA, and Furnace AA Analyses

1.0 Scope and Application

- 1.1 This Medium Level digestion procedure is an acid digestion procedure used to prepare aqueous samples for analysis using furnace atomic absorption spectroscopy (AAS), flame AAS, and/or inductively coupled plasma spectroscopy (ICP). Samples prepared using this method may be analyzed using AAS and/or ICP for the following target analyte metals:

Aluminum	Chromium	Potassium
Antimony	Cobalt	Selenium
Arsenic	Copper	Silver
Barium	Iron	Sodium
Beryllium	Lead	Thallium
Cadmium	Magnesium	Vanadium
Calcium	Manganese	Zinc
	Nickel	

1.2 Application of the Medium Level Digestion Procedure:

- 1.2.1 The Medium Level digestion procedure must be used to digest Medium Level aqueous samples.
- 1.2.2 The Medium Level digestion procedure must be used to digest Low Level aqueous samples when the Low Level CRQL requirements (Exhibit C) are achieved using the Medium Level digestion procedure and the most sensitive instrumental technique among those specified in Exhibit D; and sample preconcentration is, therefore, not required to achieve the Low Level CRQL requirements.
- 1.2.3 The Medium Level digestion method may also be used in the following circumstance, as specified in Part B, Section 2.3.1. For the target analytes in the preconcentrated digestate (from the Low Level digestion) which do not require preconcentration to achieve the Low Level CRQL requirements, a separate digestion may be performed using the Medium Level digestion procedure. The Contractor must have sufficient raw sample in order to use this option. If there is insufficient raw sample to digest another 100 mL sample volume by the Medium Level digestion method, then the Contractor may digest a reduced sample volume but no less than 50 mL. However, all reagent volumes used for the Medium Level digestion procedure must also be reduced proportionately. The sample shall be heated at 92-95°C for 2 hours or until the sample volume is reduced to approximately 25 mL. The final digestate volume must be equal to the initial sample volume.

2.0 Summary of Method

- 2.1 A 100 mL volume of well-mixed sample is digested in nitric acid and hydrogen peroxide for furnace AA analysis, and/or nitric acid and hydrochloric acid for ICP/flame AA analysis. The sample is heated, reduced to 25-50 mL, filtered, and adjusted back to the original sample volume of 100 mL.
- 2.2 The initial sample volume and final digestate volume are 100 mL. Thus, this digestion method results in no preconcentration or dilution of the original sample.

3.0 Apparatus and Materials

- 3.1 250 mL beaker or other appropriate heating vessel
- 3.2 Watch glasses
- 3.3 Thermometer that covers range of 0° to 200°C
- 3.4 Whatman No. 42 filter paper or equivalent

4.0 Reagents

- 4.1 ASTM Type II water (ASTM D1193): Water must be monitored.
- 4.2 Concentrated nitric acid (sp. gr. 1.41)
- 4.3 Concentrated hydrochloric acid (sp. gr. 1.19)
- 4.4 Hydrogen Peroxide (30%)

5.0 Sample Preservation and Handling

- 5.1 Soil/sediment (nonaqueous) samples must be refrigerated at 4°C (±2°) from receipt until analysis.

6.0 Medium Level Acid Digestion Procedure for Furnace AA Analyses of Aqueous Samples

- 6.1 Shake the sample and transfer 100 mL of well-mixed sample to a 250 mL heating vessel.
- 6.2 Add 1 mL of (1:1) HNO₃ and 2 mL 30% H₂O₂ to the sample.
- 6.3 Cover with a watch glass or similar cover and heat on a steam bath, hot plate or equivalent heating source which is adjustable and capable of maintaining a temperature of 92-95°C for 2 hours or until the sample volume is reduced to between 25 and 50 mL. Make certain that the sample does not boil.
- 6.4 Cool the sample and filter to remove insoluble material. Adjust the sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis.
- 6.5 If antimony is to be determined by furnace AA, use the digestate prepared for ICP/flame AA analysis.

7.0 Medium Level Acid Digestion Procedure for ICP/Flame AA Analyses of Aqueous Samples (Medium and Low Level)

- 7.1 Shake the sample and transfer 100 mL of well-mixed sample to a 250 mL heating vessel.
- 7.2 Add 2 mL of (1:1) HNO₃ and 10 mL of (1:1) HCl to the sample.
- 7.3 Cover with a watch glass or similar cover and heat on a steam bath, hot plate or equivalent heating source which is adjustable and capable of maintaining a temperature of 92-95°C for 2 hours or until the sample volume is reduced to between 25 and 50 mL. Make certain that the sample does not boil.
- 7.4 Cool the sample and filter to remove insoluble material. Adjust the sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis.

PART B - LOW LEVEL DIGESTION PROCEDURE FOR AQUEOUS SAMPLES (LOW LEVEL)

Sample Digestion and Preconcentration Method
for Low Level Aqueous Samples
for Analyses using Furnace AAS, Flame AAS, and/or ICP

1.0 Scope and Application

- 1.1 This method is an acid digestion and preconcentration procedure used to prepare Low Level aqueous samples for analyses of the target analytes using furnace atomic absorption spectroscopy (AAS), flame AAS, and/or inductively coupled plasma spectroscopy (ICP). Samples prepared using this method shall be analyzed using AAS and/or ICP for the following target analytes:

Aluminum	Chromium	Potassium
Antimony	Cobalt	Selenium
Arsenic	Copper	Silver
Barium	Iron	Sodium
Beryllium	Lead	Thallium
Cadmium	Magnesium	Vanadium
Calcium	Manganese	Zinc
	Nickel	

- 1.2 The Contractor shall use this Low Level digestion procedure only when the method detection limit (MDL) for a target analyte does not achieve the Low Level Contract Required Quantitation Limit (CRQL) requirements of Exhibit C using either the Medium Level digestion procedure (Part A) or the microwave digestion procedure (Part D) and the most sensitive instrumental technique among those specified in Exhibit D (i.e., ICP, flame AA, furnace AA); and sample preconcentration is, therefore, required in order for the MDL to achieve the Low Level CRQL requirements. Using this preconcentration method, the maximum allowable preconcentration factor for the sample digestate is four (i.e., 100 mL initial sample volume and 25 mL final digestate volume).
- 1.3 Using the Medium Level (or microwave) digestion procedure and the instrumental techniques specified in Exhibit D (i.e., ICP, flame AA, furnace AA), if the MDLs for all target analytes achieve their respective Low Level CRQL requirements, then the Contractor shall not use this preconcentration procedure for Low Level aqueous samples. The Contractor shall utilize the Medium Level (or microwave) digestion procedure for that instrumental technique as specified in Exhibit D, Section III. All QA/QC requirements specified in Exhibit E must be achieved.
- 1.4 Before using this Low Level digestion procedure, the Contractor must first determine and evaluate the MDLs using the most sensitive instrumental technique specified in Exhibit D to determine whether the Contractor can achieve the Low Level CRQL requirements without preconcentration. Only after the Contractor determines that the Low Level CRQL requirement still cannot be achieved for a target analyte using the Medium Level (or microwave) digestion procedure and the most sensitive instrumental technique specified in Exhibit D, shall the Contractor use this Low Level digestion procedure. The Contractor must demonstrate with their MDL studies that MDLs do not achieve the Low Level CRQL requirements (Exhibit C) using the most sensitive instrumental technique in Exhibit D and the Medium Level digestion procedure. If preconcentration is required, then the Contractor must also demonstrate with their MDL studies, as specified in Exhibit E, that the MDLs achieve the Low Level CRQL requirements using the preconcentration procedure.

For example, if the Contractor's MDL for the analysis of copper by ICP does not achieve the Low Level CRQL requirements using the Medium Level digestion procedure (no preconcentration), then the Contractor must evaluate whether the Low Level CRQL requirement can be achieved using the furnace AA technique for copper, as specified in Exhibit D, and the Medium Level digestion procedure. If the Contractor's MDL for the analysis of copper by furnace AA (using the Medium Level digestion procedure) also does not achieve the Low Level CRQL requirement, only then shall the Contractor use the Low Level digestion method

(preconcentration). Otherwise, if copper's MDL by furnace AA achieves the Low Level CRQL requirement without preconcentration, then the Contractor must use the Medium Level (or microwave) digestion procedure for furnace AA, and the method of analysis for copper must be furnace AA.

- 1.5 If the method detection limit for a target analyte does not achieve the Low Level CRQL requirement using the Medium Level (or microwave) digestion procedure and the most sensitive instrumental technique specified in Exhibit D, then the Contractor shall use the Low Level digestion procedure only if the MDLs demonstrate that the Low Level CRQL requirements are achieved using preconcentration. To minimize the extent of the preconcentration, the Contractor shall use the instrumental technique which yields the lowest MDL for that target analyte.

For example, the Contractor determines that arsenic, lead, selenium, and thallium are to be analyzed using furnace AA. The MDLs for these analytes using the furnace AA achieve the Low Level CRQL requirements except for lead (and the lead MDL using ICP also does not achieve the CRQL criteria). Therefore, lead requires preconcentration in order to achieve the Low Level CRQL criteria. Because the lead MDL is lower using furnace AA rather than ICP, the Contractor must use the furnace AA sample digestion and preconcentration procedure for Low Level aqueous samples and analyze those samples for lead using furnace AA.

2.0 Summary of Method

- 2.1 This method contains sample digestion and preconcentration procedures for Low Level aqueous samples for the furnace AA instrumental technique and for the ICP and flame AA instrumental techniques (the same digestate is used for both ICP and flame AA).
- 2.2 A well-mixed 100 mL volume of aqueous sample is digested in nitric acid and hydrogen peroxide for analyses using furnace AA, and/or nitric acid and hydrochloric acid for analyses using ICP and/or flame AA. (NOTE: If antimony is analyzed using furnace AA, then use the digestate prepared for ICP/flame AA analyses. Hydrochloric acid in the ICP/flame AA digestate facilitates antimony solubilization.) The sample is heated, reduced to 15-20 mL, and filtered.
 - 2.2.1 The Contractor then determines, based on the method detection limits, the preconcentration factor required to achieve the Low Level CRQL criteria and, thus, the final volume to which the reduced digestate is adjusted. The preconcentration factor for the sample digestate shall not exceed four, which is equivalent to an initial 100 mL sample volume and a final digestate volume of 25 mL.
- 2.3 For those target analytes in the preconcentrated digestate which do not require preconcentration to achieve the Low Level CRQL requirements, the Contractor shall follow one of two options as specified in Sections 2.3.1 and 2.3.2.

Exhibit D -- Section III
Part B - Low Level Digestion Procedure

- 2.3.1 Option One: For the target analytes in the preconcentrated digestate which do not require preconcentration to achieve the Low Level CRQL criteria, a separate digestion is performed using the Medium Level digestion procedure specified in Exhibit D, Section III. The Contractor must have sufficient raw sample in order to use this option. If there is insufficient raw sample to digest another 100 mL sample volume by the Medium Level digestion method, then the Contractor may digest a reduced sample volume but no less than 50 mL. However, all reagent volumes used for the Medium Level digestion procedure must also be reduced proportionately. The sample shall be heated at 92-95°C for 2 hours or until the sample volume is reduced to approximately 25 mL. The final digestate volume must be equal to the initial sample volume.
- 2.3.2 Option Two: An aliquot of the preconcentrated digestate is further adjusted to final volume so that there is no preconcentration (or dilution) of the original sample for those target analytes which do not require preconcentration to achieve the Low Level CRQL criteria. (There is no dilution of the initial 100 mL sample volume when using this procedure.)
- 2.4 The Contractor is cautioned that preconcentrating the sample also concentrates the matrix and interferences. To reduce the effects of the matrix and interferences when preconcentration is required, the Contractor shall use the lowest allowable preconcentration factor necessary to achieve the Low Level CRQL criteria for all target analytes using the most sensitive instrumental technique.
- 2.5 The Contractor must demonstrate that, using the Low Level preconcentration procedure, the Contractor is capable of meeting all QC requirements as specified in Exhibit E including demonstrating that blank contamination levels are not exceeded. The Contractor may need to utilize higher purity reagents in order to reduce blank contamination levels.
- 3.0 Apparatus and Materials
- 3.1 250 mL beaker or other appropriate heating vessel
- 3.2 Watch glasses
- 3.3 Heating vessel capable of maintaining temperatures of 92-95°C
- 3.4 Thermometer that covers a temperature range of 0-200°C
- 3.5 Whatman No. 42 filter paper or equivalent
- 4.0 Reagents
- 4.1 ASTM Type II Water (ASTM D1193): water must be monitored
- 4.2 Concentrated nitric acid (HNO₃) (sp. gr. 1.41)
- 4.3 Concentrated hydrochloric acid (HCl) (sp. gr. 1.19)
- 4.4 Reagent grade hydrogen peroxide (H₂O₂) (30%)
- 4.5 NOTE: If significant levels of impurities are detected in the blanks, use of higher purity reagents is recommended.
- 5.0 Sample Preservation and Handling
- 5.1 Aqueous samples are preserved with nitric acid to a pH less than 2 by the sampler immediately upon sample collection.
- 6.0 Low Level Digestion Procedure for Low Level Aqueous Samples
- 6.1 Low Level Acid Digestion and Preconcentration Procedure for Furnace AA Analysis of Low Level Aqueous Samples
- 6.1.1 Shake the sample and quantitatively transfer 100 mL of the well-mixed sample to a 250 mL heating vessel. Add 1 mL of (1+1) HNO₃ and 2 mL of 30% H₂O₂ to the sample. Cover with a watch glass or similar cover and heat for 2 hours on a steam bath, hot plate or equivalent heating

source which is adjustable and capable of maintaining a temperature of 92-95°C or until the sample volume is reduced to approximately 15-20 mL. Make certain the sample does not boil or the sample is not reduced to below 15 mL. Cool the reduced sample and quantitatively filter the digestate to remove insoluble material. The Contractor's method detection limits will then determine the volume to which the reduced digestate will be adjusted as described in Section 6.3.

NOTE: If antimony is to be determined by furnace AA, use the digestate prepared for ICP/flame AA analysis.

6.2 Low Level Acid Digestion and Preconcentration Procedure for ICP/Flame AA Analyses of Low Level Aqueous Samples

- 6.2.1 Shake the sample and quantitatively transfer 100 mL of the well-mixed sample to a 250 mL heating vessel. Add 2 mL of (1+1) HNO₃ and 3 mL of (1+1) HCl to the sample. Cover with a watch glass or similar cover and heat for 2 hours on a steam bath, hot plate or equivalent heating source which is adjustable and capable of maintaining a temperature of 92-95°C or until the sample volume is reduced to between 15-20 mL. Make certain the sample does not boil or the sample is not reduced to below 15 mL. Cool the reduced sample and quantitatively filter the digestate to remove insoluble material. The Contractor's method detection limits will then determine the volume to which the reduced digestate is adjusted as described in Section 6.3.

6.3 Adjusting the Reduced Digestate to Final Volume for ICP/Flame AA and Furnace AA

- 6.3.1 Once the reduced digestate from Sections 6.1 or 6.2 is cooled and filtered, the Contractor shall adjust the reduced digestate based on the Contractor's MDLs. The Contractor shall use the lowest preconcentration factor necessary in order for the MDLs to achieve the Low Level CRQL criteria for all target analytes using the most sensitive instrumental technique provided in Exhibit D (i.e., ICP, flame AA, furnace AA).
- 6.3.2 Only preconcentration factors of 1.0, 2.0 and 4.0 are permitted (a preconcentration factor of one is equivalent to no preconcentration and a preconcentration of three would result in the measurement of fractional volumes). Based on an initial 100 mL sample volume, this is equivalent to final adjusted digestate volumes of 100 mL, 50 mL, and 25 mL, respectively. The preconcentration factor is calculated using Equation 1:

EQ. 1

$$\text{Preconcentration Factor} = \frac{\text{Initial Sample Volume}}{\text{Final Digestate Volume}}$$

The preconcentration factor in Equation 1 shall be either 1.0 (equivalent to no preconcentration), 2.0, or 4.0, and shall not exceed a factor of 4.0.

- 6.3.3 Adjust the reduced digestate (from Sections 6.1 or 6.2) with distilled deionized water to the final preconcentrated digestate volume. This preconcentrated digestate is ready for analysis for those target analytes which require a preconcentration step. (Note: Calibration standards must contain the same acid strength as the samples.)
- 6.3.4 For target analytes which do not require preconcentration (because the MDLs for the most sensitive instrumental technique achieve the Low Level CRQL criteria), but for which a digestate preconcentration was performed (because at least one of the target analytes in that digestate required preconcentration in order to achieve the Low Level CRQL criteria), the Contractor shall use one of the two options specified in Sections 6.3.4.1 and 6.3.4.2.
- 6.3.4.1 Option One: For the target analytes in the preconcentrated digestate which do not require preconcentration to achieve the Low Level CRQL criteria, a separate digestion shall be performed using the Medium Level (or microwave) digestion procedure specified in

Exhibit D -- Section III
Part B - Low Level Digestion Procedure

Exhibit D, Section III. The Contractor must have sufficient raw sample in order to use option one. If there is insufficient raw sample to digest another 100 mL sample volume by the Medium Level digestion method, the Contractor may digest a reduced sample volume, but no less than 50 mL. However, all reagent volumes used for the Medium Level digestion procedure must also be reduced proportionately. The sample shall be heated at 92-95°C for 2 hours or until the sample volume is reduced to 15-25 mL. The final digestate volume must be equal to the initial sample volume.

- 6.3.4.2 Option Two: Take an aliquot of the final preconcentrated digestate volume from Section 6.3.3 and adjust the digestate with distilled deionized water to the volume which will result in a preconcentration factor of 1 (equivalent to no preconcentration of the sample). Determine the aliquot and final volumes which will result in a preconcentration factor of 1 using Equation 2:

EQ. 2,

$$\begin{aligned} V_f &= V_{al} \times \frac{V_i}{V_{pre}} \\ &= V_{al} \times PF \end{aligned}$$

where,

V_f = final volume to which the aliquot is adjusted
 V_{al} = volume of aliquot taken from final preconcentrated digestate (Section 6.3.3)
 V_i = initial sample volume (100 mL)
 V_{pre} = volume of final preconcentrated digestate (i.e., 25, 50, or 100 mL) (Section 6.3.3)
PF = Preconcentration Factor.

For example, the Contractor determines that arsenic, lead, selenium, and thallium are to be analyzed using furnace AA. With the exception of lead, the MDLs for these analytes using furnace AA and no preconcentration achieve the Low Level CRQL criteria. The Contractor performs a 2x preconcentration on the furnace AA digestate in order to achieve the Low Level CRQL criteria for lead. Thus, the reduced digestate is adjusted to a final preconcentrated digestate volume of 50 mL. The final preconcentrated digestate is ready for lead analysis. Because a preconcentration was not required to achieve the Low Level CRQL criteria for the other analytes (As, Se, Tl), 25 mL of the final preconcentrated digestate (of which there is 50 mL) is aliquoted and adjusted to a final volume of 50 mL (25 mL x PF, or 25 mL x 2), resulting in a final preconcentration factor of 1 for these three analytes. Any final volume greater than 50 mL would have resulted in a preparation dilution of the raw sample which is not permitted. The aliquot of the preconcentrated digestate shall be adjusted to volume such that there is no dilution of the raw sample.

- 6.3.5 The final prepared digestates that are ready for analysis shall have preconcentration factors of 1.0, 2.0, or 4.0, and shall not result in a dilution of the raw sample for any target analyte.

7.0 CALCULATIONS

- 7.1 The concentrations determined in the samples and reported as specified in Exhibit B shall be corrected for all preconcentration factors according to Equation 4:

EQ. 4.

$$\begin{array}{lcl} \text{Sample} & & \\ \text{Concentration, } \mu\text{g/L} & = & \frac{\text{Instrument reading, } \mu\text{g/L}}{\text{Preconcentration Factor}} \end{array}$$

Note that the preconcentration factor shall be either 1.0 (equivalent to no preconcentration), 2.0, or 4.0.

- 7.2 For every sample, analyte, and preconcentration factor, the raw data must clearly document how each sample result was obtained from the raw

data result (instrument reading), and how the preconcentration factor was calculated. All preconcentration factors must be provided in the example calculations.

- 7.3 The Contractor shall document on the sample preparation logbooks the specific digestion procedure (i.e., Low Level, Medium Level) used for each sample and target analyte as well as all initial, intermediate, and final sample preparation volumes. The Contractor shall document in the raw data all aliquot volumes used to make up the dilution factors and preconcentration factors for each target analyte in each sample.
- 7.4 As part of the deliverable (Exhibit B), the Contractor shall submit documentation showing that, for each target analyte that required preconcentration to achieve the Low Level CRQL criteria, the most sensitive instrumental technique (among those listed in Exhibit D) and the Medium Level digestion procedure was utilized before using the Low Level digestion procedure (see Section 1.4). For each target analyte that required preconcentration, the Contractor must submit the analyte's MDLs (Form X) using the most sensitive instrumental technique specified in Exhibit D for that analyte and the Medium Level digestion procedure, even if samples were not analyzed using that particular instrumental technique for that analyte. The preconcentration factor for each target analyte shall be documented on Forms I and XIV as described in Exhibit B.

PART C - SOIL/SEDIMENT/SOLID SAMPLE DIGESTION PROCEDURE

Acid Digestion Procedure for ICP, Flame AA and Furnace AA Analyses

1.0 Scope and Application

This method is an acid digestion procedure used to prepare soil, sediment, and sludge samples for analysis using flame atomic absorption spectroscopy (AAS), furnace AAS, and/or inductively coupled plasma spectroscopy (ICP). Samples prepared by this method may be analyzed using AAS and/or ICP for the following target analytes:

Aluminum	Chromium	Potassium
Antimony	Cobalt	Selenium
Arsenic	Copper	Silver
Barium	Iron	Sodium
Beryllium	Lead	Thallium
Cadmium	Magnesium	Vanadium
Calcium	Manganese	Zinc
	Nickel	

2.0 Summary of Method

A 1 g (wet weight) amount of well-mixed sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace AA analysis of Sb and the flame AA and ICP analysis of Al, As, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V and Zn. Nitric acid is employed as the final reflux acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn. A separate sample shall be dried for a percent solids determination (Section IV, Part F).

3.0 Apparatus and Materials

- 3.1 250 mL beaker or other appropriate heating vessel
- 3.2 Watch glasses
- 3.3 Thermometer that covers range of 0° to 200°C
- 3.4 Whatman No. 42 filter paper or equivalent

4.0 Reagents

- 4.1 ASTM Type II water (ASTM D1193): Water must be monitored.
- 4.2 Concentrated nitric acid (sp. gr. 1.41)
- 4.3 Concentrated hydrochloric acid (sp. gr. 1.19)
- 4.4 Hydrogen Peroxide (30%)

5.0 Sample Preservation and Handling

- 5.1 Soil/sediment (nonaqueous) samples must be refrigerated at 4°C (±2°) from the time of receipt until analysis.

6.0 Procedure

Prior to sample digestion, the percent solids of the soil/sediment sample must be determined in accordance with Section IV, Part F and the appropriate procedures must be followed for percent solids less than or equal to 30%.

- 6.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01g) a 1.0 to 1.5 g portion of sample and transfer to a beaker.
- 6.2 Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 92-95°C and reflux for 10 minutes without boiling.
- 6.3 Allow the sample to cool, add 5 mL of concentrated HNO_3 , replace the watch glass, as appropriate, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the heating vessel.
- 6.4 After the second reflux step is completed and the sample is cool, add 2 mL of Type II water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the heating vessel to the hot plate or equivalent heating source for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the heating vessel.
- 6.5 Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2 .)
- 6.6 Follow Sections 6.6.1 and 6.6.2 as appropriate.
 - 6.6.1 If the sample is being prepared for the furnace AA analysis of Sb or the flame AA or ICP analysis of Al, As, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, and Zn, add 5 mL of 1:1 HCl and 10 mL of Type II water, return the covered heating vessel to the hot plate or equivalent heating source, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with Type II water. The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3 . Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. The sample is now ready for analysis.
 - 6.6.2 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn, continue heating the acid-peroxide digestate until the volume is reduced to approximately 2 mL, add 10 mL of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute the sample to 100 mL with Type II water. The diluted digestate solution contains approximately 2% (v/v) HNO_3 . Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. For analysis, withdraw aliquots of appropriate volume, and add the required reagent or matrix modifier. The sample is now ready for analysis.

Exhibit D -- Section III
Part C - Soil/Sediment Digestion Procedure

7.0 Calculations

7.1 A separate determination of percent solids must be performed (Section IV, Part F).

7.2 The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

where,

C = Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample
S = % Solids/100

**PART D - MICROWAVE DIGESTION PROCEDURE FOR AQUEOUS (MEDIUM AND LOW LEVEL)
AND SOIL/SEDIMENT SAMPLES**

1.0 Scope and Application

- 1.1 This method is an acid digestion procedure using microwave energy to prepare water and soil samples for analysis by furnace AA, flame AA, and/or ICP for the following target analytes:

Aluminum	Chromium	Potassium
Antimony*	Cobalt	Selenium
Arsenic	Copper	Silver
Barium	Iron	Sodium
Beryllium	Lead	Thallium
Cadmium	Magnesium	Vanadium
Calcium	Manganese	Zinc
	Nickel	

*NOTE: This microwave digestion method shall not be used for the digestion of soil/sediment samples for the analysis of antimony.

- 1.2 This microwave digestion method may be used to digest soil/sediment samples and Medium and Low Level aqueous samples as long as MDLs achieve the CRQL requirements (Exhibit C).

2.0 Summary of Method

2.1 Water Sample Preparation:

A 45 mL volume of well-mixed water sample is digested in 5 mL of concentrated nitric acid in a Teflon^R PFA vessel for 20 minutes using microwave heating. The digestate is then filtered to remove insoluble material.

2.2 Soil Sample Preparation:

A 0.5 g (wet weight) amount of well-mixed sample is digested in 10 mL of concentrated nitric acid in a Teflon^R PFA vessel for 10 minutes using microwave heating. The digestate is then filtered to remove insoluble material. NOTE: This microwave digestion method shall not be used to digest soil/sediment samples for antimony analysis.

3.0 Apparatus and Materials

- 3.1 Commercial kitchen or home-use microwave ovens shall not be used for the digestion of samples under this contract. The oven cavity must be corrosion resistant and well ventilated. All electronics must be protected against corrosion for safe operation.
- 3.2 Microwave oven with programmable power settings up to at least 600 Watts.
- 3.3 The system must use PFA Teflon^R digestion vessels (120 mL capacity) capable of withstanding pressures of up to 110 \pm 10 psi (7.5 \pm 0.7 atm). These vessels are capable of controlled pressure relief at pressures exceeding 110 psi.
- 3.4 A rotating turntable must be used to ensure homogeneous distribution of microwave radiation within the oven. The speed of the turntable must be a minimum of 3 rpm.

Exhibit D -- Section III
Part D - Microwave Digestion Procedure

- 3.5 Polymeric volumetric ware in plastic (Teflon[®] or polyethylene) 50 mL or 100 mL capacity.
- 3.6 Whatman No. 41 filter paper (or equivalent).
- 3.7 Disposable polypropylene filter funnel.
- 3.8 Analytical balance, 300 g capacity, and minimum ± 0.01 g.
- 3.9 Polyethylene bottles, 125 mL, with caps.
- 4.0 Reagents
- 4.1 ASTM Type II water (ASTM D1193): Water must be monitored and the results of the monitor must be recorded in a logbook.
- 4.2 Nitric acid, Sub-boiled, concentrated (sp. gr. 1.41).
- 4.3 Hydrochloric acid, concentrated (sp. gr. 1.19).
- 5.0 Microwave Calibration Procedure
- 5.1 The calibration procedure is a critical step prior to the use of any microwave unit. The microwave unit must be calibrated every six months. The calibration data for each calibration must be submitted to EPA upon request and available for review during on-site audits. In order that absolute power settings may be interchanged from one microwave unit to another, the actual delivered power must be determined. Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between the output power and the scale used in controlling the microwave unit, then the calibration can be a two-point calibration at maximum and 40% power. If the unit is not accurate or precise for some portion of the controlling scale, then a multiple-point calibration is necessary. If the unit power calibration needs a multiple-point calibration, then the point where linearity begins must be identified. For example, a calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, 50 and 40% power settings can be applied and the data plotted. The non-linear portion of the calibration curve can be excluded or restricted in use. Each percent is equivalent to approximately 5.5-6 watts and becomes the smallest unit of power that can be controlled. If 20-40 watts are contained from 99-100%, that portion of the microwave calibration is not controllable by 3-7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in that portion of the power scale.
- 5.2 The power available for heating is evaluated so that the absolute power setting (watts) may be compared from one microwave to another. This is accomplished by measuring the temperature rise in 1 Kg of water exposed to microwave radiation for a fixed period of time. The water is placed in a Teflon[®] beaker (or a beaker that is made of some other material that does not adsorb microwave energy) and stirred before measuring the temperature. Glass beakers adsorb microwave energy and may not be used. The initial temperature of the water must be between 19 and 25 °C. The beaker is circulated continuously through the field for at least two (2) minutes at full power. The beaker is removed from the microwave, the water is stirred vigorously, and the final temperature is recorded. The final reading is the maximum temperature reading after each energy exposure. These measurements must be accurate to $\pm 0.1^{\circ}\text{C}$ and made within 30 seconds of the end of heating. If more measurements are needed, do not use the same water until it has cooled down to room temperature. Otherwise, use a fresh water sample.

5.3 The absorbed power is determined using Equation 1:

EQ. 1,

$$P = \frac{(K) (C_p) (m) (DT)}{t}$$

where,

P = The apparent power absorbed by the sample in watts (joules per second),
K = The conversion factor for thermochemical calories per second to watts (= 4.184),
C_p = The heat capacity, thermal capacity, or specific heat (cal. g⁻¹.°C⁻¹) of water (=1.0),
m = The mass of the sample in grams (g),
DT = The final temperature minus the initial temperature (°C), and
t = The time in seconds (s).

Using 2 minutes and 1 Kg of distilled water, the calibration equation simplifies to:

$$P = (DT) (34.87).$$

The microwave user can now relate power in watts to the percent power setting of the microwave.

6.0 Cleaning Procedure

6.1 The initial cleaning of the PFA vessels:

- 6.1.1 Prior to first use - new vessels must be annealed before they are used. A pretreatment/cleaning procedure must be followed. This procedure calls for heating the vessels for 96 hours at 200°C. The vessels must be disassembled during annealing and the sealing surfaces (the top of the vessel or its rim) must not be used to support the vessel during annealing.
 - 6.1.2 Rinse in ASTM Type I water.
 - 6.1.3 Immerse in 1:1 HCl for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.
 - 6.1.4 Rinse in ASTM Type I water.
 - 6.1.5 Immerse in 1:1 HNO₃ for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.
 - 6.1.6 The vessels are then rinsed with copious amounts of ASTM Type I water prior to use for any analyses under this contract.
- 6.2 Cleaning procedure between sample digestions:
- 6.2.1 Wash entire vessel in hot water using laboratory-grade nonphosphate detergent.
 - 6.2.2 Rinse with 1:1 nitric acid.
 - 6.2.3 Rinse three times with ASTM Type I water. If contaminants are found in the preparation blank, it is mandatory that steps 6.1.2 through 6.1.6 be strictly adhered to.

Exhibit D -- Section III
Part D - Microwave Digestion Procedure

7.0 Water Digestion Procedure

- 7.1 A 45 mL aliquot of the sample is measured into Teflon[®] digestion vessels using volumetric glassware.
- 7.2 A 5 mL volume of high purity concentrated HNO₃ is added to the digestion vessels.
- 7.3 The caps (with pressure release valves) are placed on the vessels hand tight and then tightened using constant torque to 12 ft./lbs. The weight of each vessel is recorded to 0.02 g.
- 7.4 Place 5 sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. Venting tubes connect each sample vessel with a collection vessel. Each sample vessel is attached to a clean, double-ported vessel to collect any sample expelled from the sample vessel in the event of over pressurization. Assembly of the vessels into the carousel may be done inside or outside the microwave.
- 7.5 This procedure is energy balanced for five 45 mL water samples (each with 5 mL of acid) to produce consistent conditions. When fewer than 5 samples are digested, the remaining vessels must be filled with 45 mL of tap, DI or Type II water and 5 mL of concentrated nitric acid.
- Newer microwave ovens may be capable of higher power settings which may allow a larger number of samples. If the analyst wishes to digest more than 5 samples at a time, the analyst may use different power settings as long as they result in the same time temperature conditions defined in the power programming for this method.
- 7.6 The initial temperature of the samples should be $24 \pm 1^{\circ}\text{C}$. The preparation blank must have 45 mL of deionized water and the same amount (5 mL) of acid that is added to the samples.
- 7.7 The microwave unit first-stage program must be set to give 545 watts for 10 minutes and the second-stage program to give 344 watts for 10 minutes. This sequence brings the samples to $160 \pm 4^{\circ}\text{C}$ in ten minutes and permits a slow rise to 165-170°C during the second 10 minutes.
- 7.8 Following the 20 minute program, the samples are left to cool in the microwave unit for five minutes, with the exhaust fan ON. The samples and/or carousel may then be removed from the microwave unit. Before opening the vessels, let cool until they are no longer hot to the touch.
- 7.9 After the sample vessel has cooled, weigh the sample vessel and compare to the initial weight as reported in the preparation log. Any sample vessel exhibiting a ≤ 0.50 g loss must have any excess sample from the associated collection vessel added to the original sample vessel before proceeding with the sample preparation. Any sample vessel exhibiting a > 0.50 g loss must be identified in the preparation log and the sample redigested.
- 7.10 Sample Filtration: The digested samples are shaken well to mix in any condensate within the digestion vessel before being opened. The digestates are then filtered into 50 mL glass volumetric flasks through ultra-clean filter paper and diluted to 50 mL (if necessary). The samples are now ready for analysis. The sample results must be corrected by a factor of 1.11 in order to report final concentration values based on an initial volume of 45 mL. Concentrations so determined shall be reported as "total."

8.0 Soil Sample Digestion Procedure

Prior to sample digestion, the percent solids of the soil/sediment sample must be determined in accordance with Section IV, Part F and the appropriate procedures must be followed for percent solids less than or equal to 30%.

- 8.1 Add a representative 0.5 \pm 0.050 grams of sample to the Teflon^R PFA vessel.
- 8.2 Add 10 \pm 0.1 mL of concentrated nitric acid. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel.
- 8.3 Cap the vessel, then tighten using constant torque to 12 ft/lbs, according to the manufacturer's direction.
- 8.4 Connect the sample vessel to the overflow vessel using Teflon^R PFA tubing.
- 8.5 Weigh the vessel assembly to the nearest 0.01 g.
- 8.6 Place sample vessels in groups of 2 sample vessels or 6 sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. If fewer than the recommended number of samples are to be digested (i.e., 3 samples plus 1 blank) then the remaining vessels must be filled with 10 mL of nitric acid to achieve the full complement of vessels.
- 8.7 Each sample vessel must be attached to a clean, double-ported vessel to collect any sample expelled from the sample vessel in the event of over pressurization. Assembly of the vessels into the carousel may be done inside or outside the microwave. Connect the overflow vessel to the center well of the oven.
- 8.8 The preparation blank must have 0.5 mL of deionized water and the same amount (10 mL) of acid that is added to the samples. The preparation blank must later be diluted to 50 mL in the same manner as the samples.
- 8.9 Irradiate the 2 sample vessel group at 344 watts for 10 minutes, or the 6-sample vessel group at 574 watts for 10 minutes.

This program brings the samples to 175°C in 5.5 minutes; the temperature remains between 170-180°C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most samples. The pressure may exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases, the pressure will be limited by the relief pressure of the vessel to 7.5 \pm 0.7 atm.
- 8.10 Allow the vessels to cool for a minimum of five minutes before removing them from the microwave unit, with exhaust fan ON. Allow the vessels to cool to room temperature before opening. The vessels must be carefully vented and uncapped in a fume hood.
- 8.11 Weigh each vessel assembly. If the weight of acid plus the sample has decreased by more than 10% from the original weight, discard the digests. Determine the reason for the loss. Losses typically are attributed to use of digestion time longer than ten minutes, using too large of a sample, or having improper heating conditions. Once the source of the losses has been corrected, prepare a new set of samples for digestion.

Exhibit D -- Section III
Part D - Microwave Digestion Procedure

- 8.12 Sample Filtration: Shake the sample well to mix in any condensate within the digestion vessel before being opened. Filter the digestion vessel into a 50 mL glass volumetric flask through ultra-clean filter paper. Rinse the sample digestion vessel, cap, connecting tube, and (if venting occurred) the overflow vessel into the 50 mL glass flask. Dilute to 50 mL. The samples are now ready for analysis. Concentrations so determined shall be reported as "total."

9.0 Calculations

- 9.1 The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample using Equation 2:

EQ. 2,

$$\text{Concentration (dry wt.) (mg/Kg)} = \frac{C \times V}{W \times S}$$

where,

C = Concentration (mg/L),
V = Final volume in liters after sample
preparation,
W = Weight in Kg of wet sample,
S = % Solids/100

PART E. MERCURY SAMPLE PREPARATION

Refer to each specific method in Exhibit D, Section IV, Part D.

PART F. CYANIDE SAMPLE PREPARATION

Refer to each specific method in Exhibit D, Section IV, Part E.

PART G. TOTAL ORGANIC CARBON SAMPLE PREPARATION

Refer to each specific method in Exhibit D, Section IV, Part G.

PART H. TOTAL COMBUSTIBLE ORGANICS SAMPLE PREPARATION

Refer to each specific method in Exhibit D, Section IV, Part H.

PART I. GRAIN SIZE DISTRIBUTION SAMPLE PREPARATION

Refer to each specific method in Exhibit D, Section IV, Part I.

SECTION IV

SAMPLE ANALYSIS

	<u>Page No.</u>
Part A - Inductively Coupled Plasma-Atomic Emission Spectrophotometric Method	D-29
Part B - Atomic Absorption Methods, Furnace Technique	D-39
Part C - Atomic Absorption Methods, Flame Technique	D-54
Part D - Cold Vapor Methods for Mercury Analysis	D-59
Part E - Methods for Total Cyanide Analysis	D-72
Part F - Percent Solids Determination Procedure	D-91
Part G - Total Organic Carbon in Aqueous and Soil/Sediment Samples .	D-93
Part H - Total Combustible Organics in Soil/Sediment Samples	D-120
Part I - Grain Size Distribution in Soil/Sediment Samples	D-128

PART A - INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROPHOTOMETRIC METHOD

Method 200.7 REAP-M*
INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROPHOTOMETRIC METHOD
FOR TRACE ELEMENT ANALYSIS OF AQUEOUS AND SOIL/SEDIMENT SAMPLES

1.0 Scope and Application

- 1.1 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. This is especially true when dissolved solids exceed 1500 mg/L. (See Section 4.0)
- 1.2 Table 1 lists elements along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detected limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.
- 1.3 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

2.0 Summary of Method

The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by a photosensitive device. The photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 4.1 (and tests for their presence as described in Section 4.2) should also be recognized and appropriate corrections made.

3.0 Safety

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should be made available to all personnel involved in the chemical analysis.

4.0 Interferences

- 4.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:
- 4.1.1 Spectral interferences can be categorized as 1) overlap of a spectral line from another element; 2) unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination

*REAP-M modified for the Regional Environmental Analytical Procurement.

phenomena; and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array.

Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The interference information, which was collected at the Ames Laboratory**, is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interferent element.

The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system. Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed from the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths is not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

- 4.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift.

Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution has been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

- 4.1.3 Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

**Ames Laboratory, USDOE, Iowa State University, Ames, Iowa 50011.

- 4.2 Prior to reporting concentration data for the analyte elements, the Contractor shall analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis shall be performed on a sample from each group of samples of a similar matrix type and concentration or for each Sample Delivery Group, whichever is more frequent. Samples identified as equipment blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the method detection limit in the original sample), the serial dilution (a five fold dilution) shall then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E" on FORM IX and FORM I.

5.0 Apparatus

5.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

5.1.1 Computer controlled atomic emission spectrometer with background correction.

5.1.2 Radio frequency generator.

5.1.3 Argon gas supply, welding grade or better.

5.2 Operating conditions - Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where correction factors are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

6.0 Reagents and Standards

- 6.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.
- 6.1.1 Acetic acid, concentrated (sp gr 1.06).
- 6.1.2 Hydrochloric acid, concentrated (sp gr 1.19).
- 6.1.3 Hydrochloric acid, (1+1): Add 500 mL concentrated HCl (sp gr 1.19) to 400 mL deionized, distilled water and dilute to 1 liter.
- 6.1.4 Nitric acid, concentrated (sp gr 1.41).
- 6.1.5 Nitric acid, (1+1): Add 500 mL concentrated HNO₃ (sp gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.
- 6.2 Deionized, distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents and calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193.
- 6.3 Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 hour at 105° C unless otherwise specified. (**CAUTION:** Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow:
- 6.3.1 Aluminum solution, stock, 1 mL = 100 ug Al: Dissolved 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of concentrated HNO₃ in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HCl and dilute to 1000 mL with deionized, distilled water.
- 6.3.2 Antimony solution stock, 1 mL = 100 ug Sb: Dissolve 0.2669 g K(SbO)C₄H₄O₆ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1000 mL with deionized, distilled water.
- 6.3.3 Arsenic solution, stock, 1 mL = 100 ug As: Dissolve 0.1320 g of As₂O₃ in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO₃ and dilute to 1,000 mL with deionized, distilled water.
- 6.3.4 Barium solution, stock, 1 mL = 100 ug Ba: Dissolve 0.1516 g BaCl₂ (dried at 250°C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.
- 6.3.5 Beryllium solution, stock, 1 mL = 100 ug Be: Do not dry. Dissolve 1.966 g BeSO₄·4H₂O, in deionized, distilled water, add 10.0 mL concentrated HNO₃ and dilute to 1,000 mL with deionized, distilled water.
- 6.3.6 Cadmium solution, stock, 1 mL = 100 ug Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ and dilute to 1,000 mL with deionized, distilled water.

- 6.3.7 Calcium solution, stock, 1 mL = 100 ug Ca: Suspend 0.2498 g CaCO_3 dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3 . Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 6.3.8 Chromium solution, stock, 1 mL = 100 ug Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete acidify with 10 mL concentrated HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 6.3.9 Cobalt solution stock, 1 mL = 100 ug Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3 . Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.
- 6.3.10 Copper solution, stock, 1 mL = 100 ug Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3 . Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 6.3.11 Iron solution, stock, 1 mL = 100 ug Fe: Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of concentrated HNO_3 . Cool, add an additional 5 mL of concentrated HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 6.3.12 Lead solution, stock, 1 mL = 100 ug Pb: Dissolve 0.1599 g $\text{Pb}(\text{NO}_3)_2$ in a minimum amount of (1+1) HNO_3 . Add 10.0 mL of concentrated HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 6.3.13 Magnesium solution, stock, 1 mL = 100 ug Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3 . Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 6.3.14 Manganese solution, stock, 1 mL = 100 ug Mn: Dissolve 0.1000 g of manganese metal in the acid mixture, 10 mL concentrated HCl and 1 mL concentrated HNO_3 , and dilute to 1,000 mL with deionized, distilled water.
- 6.3.15 Nickel solution, stock, 1 mL = 100 ug Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot concentrated HNO_3 , cool and dilute to 1,000 mL with deionized, distilled water.
- 6.3.16 Potassium solution, stock, 1 mL = 100 ug K: Dissolve 0.1907 g KCl , dried at 110°C, in deionized, distilled water. Dilute to 1,000 mL.
- 6.3.17 Selenium solution, stock, 1 mL = 100 ug Se: Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.
- 6.3.18 Silver solution, stock, 1 mL = 100 ug Ag: Dissolve 0.1575 g AgNO_3 in 100 mL of deionized, distilled water and 10 mL concentrated HNO_3 . Dilute to 1,000 mL with deionized, distilled water.
- 6.3.19 Sodium solution, stock, 1 mL = 100 ug Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 6.3.20 Thallium solution, stock, 1 mL = 100 ug Tl: Dissolve 0.1303 g TlNO_3 in deionized, distilled water. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 6.3.21 Vanadium solution, stock, 1 mL = 100 ug V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of concentrated HNO_3 . Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 6.3.22 Zinc solution, stock, 1 mL = 100 ug Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3 . Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 6.4 Mixed calibration standard solutions -- Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See Sections 6.4.1 through 6.4.5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl and dilute to 100 mL with deionized, distilled water. (See NOTE in Section 6.4.5.) Prior to

preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (see Section 6.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

- 6.4.1 Mixed standard solution I -- Manganese, beryllium, cadmium, lead, and zinc.
- 6.4.2 Mixed standard solution II -- Barium, copper, iron, vanadium, and cobalt.
- 6.4.3 Mixed standard solution III -- Arsenic and selenium.
- 6.4.4 Mixed standard solution IV -- Calcium, sodium, potassium, aluminum, chromium and nickel.
- 6.4.5 Mixed standard solution V -- Antimony, magnesium, silver, and thallium.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

- 6.5 Two types of blanks are required for the analysis. The calibration blank (see Exhibit E) is used in establishing the analytical curve while the reagent blank (preparation blank, Exhibit E) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.
 - 6.5.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO₃ and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

- 6.5.2 The reagent blank (or preparation blank - see Exhibit E) must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.
- 6.6 In addition to the calibration standards, an instrument check standard, an interference check sample and a quality control sample are also required for the analyses (see Exhibit E).
 - 6.6.1 The instrument check standard for continuing calibration verification is prepared by the analyst by combining compatible elements at a concentration equivalent to the mid-points of their respective calibration curves.
 - 6.6.2 The interference check sample is prepared by the analyst, or obtained commercial vendors.
 - 6.6.3 The quality control sample for the initial calibration verification must be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier.
- 7.0 Procedure
 - 7.1 Set up instrument with proper operating parameters established in Section 5.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.
 - 7.2 Initiate appropriate operating configuration of computer.
 - 7.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using mixed calibration standard solutions such as those described in Section 6.4. A peristaltic pump must be used to introduce all solutions to the nebulizer. Flush the system with the calibration blank (Section 6.5.1) between each standard.
 - 7.4 Begin the sample run flushing the system with the calibration blank solution (Section 6.5.1) between each sample. Analyze the instrument check standard (Section 6.6.1) and the calibration blank (Section 6.5.1) each 10 analytical samples.
 - 7.5 A minimum of two replicate exposures is required for standardization and all QC and sample analyses. The average result of the multiple exposures for the standardization and all QC and sample analyses shall be used.
- 8.0 Calculation
 - 8.1 If dilutions were performed, the appropriate factor shall be applied to sample values.
 - 8.2 Units shall be clearly specified.
- 9.0 Quality Control
 - 9.1 Quality control shall be performed as specified in Exhibit E.

TABLE 1 - RECOMMENDED WAVELENGTHS AND ESTIMATED
INSTRUMENTAL DETECTION LIMITS

Element	Wavelength, nm(1)	Estimated Detection Limit, ug/L(2)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Nickel	231.604	15
Potassium	766.491	See(3)
Selenium	196.026	75
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

- (1) The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See Section 4.1.1.) The use of alternate wavelengths must be reported (in nm) with the sample data.
- (2) The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.
- (3) Highly dependent on operating conditions and plasma position.

TABLE 2. EXAMPLE OF ANALYTE CONCENTRATION EQUIVALENTS (MG/L) ARISING FROM INTERFERENTS AT THE 100 MG/L LEVEL

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

TABLE 3

INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED
FOR INTERFERENCE MEASUREMENTS IN TABLE 2

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

PART B - ATOMIC ABSORPTION METHODS, FURNACE TECHNIQUE***

Table of Contents

<u>Analyte/Method</u>	<u>Page No.</u>
Antimony - Method 204.2 REAP-M*	D-40
Arsenic - Method 206.2 REAP-M	D-41
Beryllium - Method 210.2 REAP-M	D-43
Cadmium - Method 213.2 REAP-M	D-44
Chromium - Method 218.2 REAP-M	D-45
Copper - Method 220.2 REAP-M	D-46
Lead - Method 239.2 REAP-M	D-47
Nickel - Method 249.2 REAP-M	D-49
Selenium - Method 270.2 REAP-M	D-50
Silver - Method 272.2 REAP-M	D-52
Thallium - Method 279.2 REAP-M	D-53

*From "Methods for Chemical Analysis of Water and Wastes" (EPA-600/4-79-020), Metals-4, as modified for use in the Regional Environmental Analytical Procurement.

*REAP-M modified for the Regional Environmental Analytical Procurement.

ANTIMONY
Method 204.2 REAP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 20-300 ug/L
Approximate Detection Limit: 3 ug/L

1.0 Preparation of Standard Solution

- 1.1 Stock solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 liter with deionized water. 1 mL = 1 mg Sb (1000 mg/L).
- 1.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for method of standard additions.
- 1.3 The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

2.0 Instrument Parameters (General)

- 2.1 Drying Time and Temp: 30 sec @ 125°C.
- 2.2 Ashing Time and Temp: 30 sec @ 800°C.
- 2.3 Atomizing Time and Temp: 10 sec @ 2700°C.
- 2.4 Purge Gas Atmosphere: Argon
- 2.5 Wavelength: 217.6 nm
- 2.6 Operating parameters should be set as specified by the particular instrument manufacturer.

3.0 Notes

- 3.1 The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
- 3.2 The use of background correction is required.
- 3.3 Nitrogen may also be used as the purge gas.
- 3.4 If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.
- 3.5 For every sample analyzed, verification is necessary to determine that method of standard additions is not required (see Exhibit E).
- 3.6 If method of standard additions is required, follow the procedure given in Exhibit E.

*REAP-M modified for the Regional Environmental Analytical Procurement.

ARSENIC

Method 206.2 REAP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

1.0 Preparation of Standard Solution

- 1.1 Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 mL of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter. 1 mL = 1 mg As (1000 mg/l).
- 1.2 Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized distilled water and make up to 100 mL.
- 1.3 Nickel Nitrate Solution, 1%: Dilute 20 mL of the 5% nickel nitrate to 100 mL with deionized distilled water.
- 1.4 Working Arsenic Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, and add 1 mL of concentrated HNO_3 , 2 mL of 30% H_2O_2 and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with deionized distilled water.

2.0 Sample Preparation

- 2.1 Add 100 uL of the 5% nickel nitrate solution to 5 mL of the digested sample. The sample is now ready for injection into the furnace.

Note: Another matrix modifier may be substituted for nickel nitrate if recommended by the instrument manufacturer. The matrix modifier used shall be reported in the SDG Case Narrative.

3.0 Instrument Parameters (General)

- 3.1 Drying Time and Temp: 30 sec @ 125°C.
- 3.2 Ashing Time and Temp: 30 sec @ 1100°C.
- 3.3 Atomizing Time and Temp: 10 sec @ 2700°C.
- 3.4 Purge Gas Atmosphere: Argon
- 3.5 Wavelength: 193.7 nm
- 3.6 Operating parameters should be set as specified by the particular instrument manufacturer.

4.0 Notes

- 4.1 The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
- 4.2 The use of background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (i.e., Al, Fe). If conditions occur where significant interference is suspected, the lab must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.
- 4.3 For every sample analyzed, verification is necessary to determine that the method of standard additions is not required (see Exhibit E).
- 4.4 If method of standard additions is required, follow the procedure given in Exhibit E.
- 4.5 The use of the Electrodeless Discharge Lamps (EDL) for the light source is recommended.

*REAP-M modified for the Regional Environmental Analytical Procurement.

BERYLLIUM

Method 210.2 REAP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 1-30 ug/L
Approximate Detection Limit: 0.2 ug/L

1.0 Preparation of Standard Solution

- 1.1 Stock solution: Dissolve 11.6586 g of beryllium sulfate, BeSO_4 , in deionized distilled water containing 2 mL concentrated nitric acid and dilute to 1 liter. 1 mL = 1 mg Be (1000 mg/L).
- 1.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for the method of standard additions.
- 1.3 The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

2.0 Instrument Parameters (General)

- 2.1 Drying Time and Temp: 30 sec @ 125°C.
- 2.2 Ashing Time and Temp: 30 sec @ 1000°C.
- 2.3 Atomizing Time and Temp: 10 sec @ 2800°C.
- 2.4 Purge Gas Atmosphere: Argon
- 2.5 Wavelength: 234.9 nm
- 2.6 Operating parameters should be set as specified by the particular instrument manufacturer.

3.0 Notes

- 3.1 The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite, and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
- 3.2 The use of background correction is required.
- 3.3 Because of possible chemical interaction, nitrogen should not be used as a purge gas.
- 3.4 For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
- 3.5 If method of standard additions is required, follow the procedure given in Exhibit E.

*REAP-M modified for the Regional Environmental Analytical Procurement.

CADMIUM

Method 213.2 REAP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 0.5-10 ug/L
Approximate Detection Limit: 0.1 ug/L

1.0 Preparation of Standard Solution

- 1.1 Stock solution: Carefully weigh 2.282 g of cadmium sulfate, $3 \text{ CdSO}_4 \cdot 8\text{H}_2\text{O}$ (analytical reagent grade) and dissolve in deionized distilled water. Make up to 1 liter with deionized distilled water. 1 mL = 1 mg Cd (1000 mg/L).
- 1.2 Ammonium Phosphate solution (40%): Dissolve 40 grams of ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 mL.
- 1.3 Prepare dilutions of stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL of the ammonium phosphate solution. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

2.0 Instrument Parameters (General)

- 2.1 Drying Time and Temp: 30 sec @ 125°C.
- 2.2 Ashing Time and Temp: 30 sec @ 500°C.
- 2.3 Atomizing Time and Temp: 10 sec @ 1900°C.
- 2.4 Purge Gas Atmosphere: Argon
- 2.5 Wavelength: 228.8 nm
- 2.6 Operating parameters should be set as specified by the particular instrument manufacturer.

3.0 Notes

- 3.1 The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite, and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
- 3.2 The use of background correction is required.
- 3.3 Contamination from the work area is critical in cadmium analysis. Use pipette tips which are free of cadmium.
- 3.4 For every sample analyzed, verification is necessary to determine that method of standard additions is not required (see Exhibit E).
- 3.5 If method of standard additions is required, follow the procedure given in Exhibit E.

*REAP-M modified for the Regional Environmental Analytical Procurement.

CHROMIUM

Method 218.2 REAP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

1.0 Preparation of Standard Solution

- 1.1 Stock solution: Dissolve 1.923 g of chromium trioxide (CrO_3 , reagent grade) in deionized distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Cr (1000 mg/L).
- 1.2 Calcium Nitrate solution: Dissolve 11.8 grams of calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (analytical reagent grade) in deionized distilled water and dilute to 100 mL. 1 mL = 20 mg Ca.
- 1.3 Prepare dilutions of the stock chromium solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of standard and sample alike, add 1 mL of 30% H_2O_2 and 1 mL of the calcium nitrate solution.

2.0 Instrument Parameters (General)

- 2.1 Drying Time and Temp: 30 sec @ 125°C.
- 2.2 Ashing Time and Temp: 30 sec @ 1000°C.
- 2.3 Atomizing Time and Temp: 10 sec @ 2700°C.
- 2.4 Purge Gas Atmosphere: Argon
- 2.5 Wavelength: 357.9 nm
- 2.6 Operating parameters should be set as specified by the particular instrument manufacturer.

3.0 Notes

- 3.1 The above concentration values and instrument conditions are for a Perkin Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite, and are to be used as guidelines only.
- 3.2 Hydrogen peroxide is added to the acidified solution to convert all chromium to the trivalent state. Calcium is added to a level above 200 mg/L where its suppressive effect becomes constant up to 1000 mg/L.
- 3.3 Background correction is required.
- 3.4 Nitrogen should not be used as a purge gas because of possible CN band interference.
- 3.5 Pipette tips have been reported to be a possible source of contamination.
- 3.6 For every sample analyzed, verification is necessary to determine that method of standard additions is not required (see Exhibit E).
- 3.7 If method of standard additions is required, follow the procedure given in Exhibit E.

*REAP-M modified for the Regional Environmental Analytical Procurement.

COPPER

Method 220.2 REAP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

1.0 Preparation of Standard Solution

- 1.1 Stock solution: Carefully weigh 100 g of electrolyte copper (analytical reagent grade). Dissolve in 5 mL redistilled HNO₃ and make up to 1 liter with deionized distilled water. Final concentration is 1 mg Cu per mL (1000 mg/L).
- 1.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."
- 1.3 The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

2.0 Instrument Parameters (General)

- 2.1 Drying Time and Temp: 30 sec @ 125°C.
- 2.2 Ashing Time and Temp: 30 sec @ 900°C.
- 2.3 Atomizing Time and Temp: 10 sec @ 2700°C.
- 2.4 Purge Gas Atmosphere: Argon
- 2.5 Wavelength: 324.7 nm
- 2.6 Other operating parameters should be set as specified by the particular instrument manufacturer.

3.0 Notes

- 3.1 The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite, and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
- 3.2 Background correction is required.
- 3.3 Nitrogen may also be used as the purge gas.
- 3.4 For every sample analyzed, verification is necessary to determine that method of standard additions is not required (see Exhibit E).
- 3.5 If method of standard additions is required, follow the procedure given in Exhibit E.

*REAP-M modified for the Regional Environmental Analytical Procurement.

LEAD

Method 239.2 REAP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

1.0 Preparation of Standard Solution

- 1.1 Stock solution: Carefully weigh 1.599 g of lead nitrate, $\text{Pb}(\text{NO}_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete, acidify with 10 mL redistilled HNO_3 and dilute to 1 Liter with deionized distilled water. 1 mL = 1 mg Pb (1000 mg/L).
- 1.2 Lanthanum Nitrate solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 mL concentrated HNO_3 and dilute to 1000 mL with deionized distilled water. 1 mL = 50 mg La.
- 1.3 Working Lead solution: Prepare dilutions of stock lead solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of diluted standard add 10 mL of the lanthanum nitrate solution.

2.0 Sample Preparation

- 2.1 To each 100 mL of prepared sample solution add 10 mL of the lanthanum nitrate solution.

Note: Another matrix modifier may be substituted for lanthanum nitrate if recommended by the instrument manufacturer. The matrix modifier used shall be reported in the SDG Case Narrative.

3.0 Instrument Parameters (General)

- 3.1 Drying Time and Temp: 30 sec @ 125°C.
- 3.2 Ashing Time and Temp: 30 sec @ 500°C.
- 3.3 Atomizing Time and Temp: 10 sec @ 2700°C.
- 3.4 Purge Gas Atmosphere: Argon
- 3.5 Wavelength: 283.3 nm
- 3.6 Operating parameters should be set as specified by the particular instrument manufacturer.

4.0 Notes

- 4.1 The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite, and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
- 4.2 The use of background correction is required.
- 4.3 Greater sensitivity can be achieved using the 217.0 nm line, but the optimum concentration range is reduced. The use of a lead electrodeless discharge lamp at this lower wavelength has been found to be advantageous. Also a lower atomization temperature (2400°C) may be preferred.
- 4.4 To suppress sulfate interference (up to 1500 ppm), lanthanum is added as the nitrate to both samples and calibration standards. (Atomic Absorption Newsletter Vol. 15, No. 3, p. 71, May-June 1976.)
- 4.5 Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.
- 4.6 For every sample analyzed, verification is necessary to determine that method of standard additions is not required (see Exhibit E).

*REAP-M modified for the Regional Environmental Analytical Procurement.

- 4.7 If method of standard additions is required, follow the procedure given in Exhibit E.

NICKEL

Method 249.2 REAP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-50 ug/L
Approximate Detection Limit: 1 ug/L

1.0 Preparation of Standard Solution

- 1.1 Stock solution: Carefully weigh 4.953 g of nickel nitrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete, acidify with 10 mL of conc. HNO_3 and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Ni (1000 mg/L).
- 1.2 Working Nickel solution: Prepare dilutions of stock nickel solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

2.0 Instrument Parameters (General)

- 2.1 Drying Time and Temp: 30 sec @ 125°C.
2.2 Ashing Time and Temp: 30 sec @ 800°C.
2.3 Atomizing Time and Temp: 10 sec @ 2700°C.
2.4 Purge Gas Atmosphere: Argon
2.5 Wavelength: 232.0 nm
2.6 Operating parameters should be set as specified by the particular instrument manufacturer.

3.0 Notes

- 3.1 The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and pyrolytic graphite, and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
- 3.2 The use of background correction is required.
- 3.3 Nitrogen may also be used as the purge gas.
- 3.4 For every sample analyzed, verification is necessary to determine that method of standard additions is not required (see Exhibit E).
- 3.5 If method of standard additions is required, follow the procedure given in Exhibit E.

*REAP-M modified for the Regional Environmental Analytical Procurement.

SELENIUM

Method 270.2 REAP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 2 ug/L

1.0 Preparation of Standard Solution

- 1.1 Stock Selenium solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 mL. 1 mL = 1 mg Se (1000 mg/L).
- 1.2 Nickel Nitrate solution, 5%: Dissolve 24.780 g of ACS reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized distilled water and make up to 100 mL.
- 1.3 Nickel Nitrate solution, 1%: Dilute 20 mL of the 5% nickel nitrate to 100 mL with deionized distilled water.
- 1.4 Working Selenium solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. Withdraw appropriate aliquots of the stock solution, and add 1 mL of concentrated HNO_3 , 2 mL of 30% H_2O_2 and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with deionized distilled water.

2.0 Sample Preparation

- 2.1 Add 100 uL of the 5% nickel nitrate solution to 5 mL of the digested sample. The sample is now ready for injection into the furnace.

Note: Another matrix modifier may be substituted for nickel nitrate if recommended by the instrument manufacturer. The matrix modifier used shall be reported in the SDG Case Narrative.

3.0 Instrument Parameters

- 3.1 Drying Time and Temp: 30 sec @ 125°C.
- 3.2 Charring Time and Temp: 30 sec @ 1200°C.
- 3.3 Atomizing Time and Temp: 10 sec @ 2700°C.
- 3.4 Purge Gas Atmosphere: Argon
- 3.5 Wavelength: 196.0 nm
- 3.6 Operating parameters should be set as specified by the particular instrument manufacturer.

4.0 Notes

- 4.1 The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, purge gas interrupt and non-pyrolytic graphite, and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
- 4.2 The use of background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (i.e., Al, Fe). If conditions occur where significant interference is suspected, the lab must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.
- 4.3 Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/L, both samples and standards should be prepared to contain 1% nickel.
- 4.4 For every sample analyzed, verification is necessary to determine that method of standard additions is not required (see Exhibit E).

*REAP-M modified for the Regional Environmental Analytical Procurement.

Exhibit D -- Section IV
Part B - Furnace AA

- 4.5 If method of standard additions is required, follow the procedure given in Exhibit E.
- 4.6 The use of the Electrodeless Discharge Lamp (EDL) for the light source is recommended.

SILVER

Method 272.2 REAP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 1-25 ug/L
Approximate Detection Limit: 0.2 ug/L

1.0 Preparation of Standard Solution

- 1.1 Stock solution: Dissolve 1.575 g of AgNO₃ (analytical reagent grade) in deionized distilled water. Add 10 mL of concentrated HNO₃ and make up to 1 liter. 1 mL = 1 mg Ag (1000 mg/L).
- 1.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for method of standard additions.
- 1.3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

2.0 Instrument Parameters (General)

- 2.1 Drying Time and Temp: 30 sec @ 125°C.
- 2.2 Ashing Time and Temp: 30 sec @ 400°C.
- 2.3 Atomizing Time and Temp: 10 sec @ 2700°C.
- 2.4 Purge Gas Atmosphere: Argon
- 2.5 Wavelength: 328.1 nm
- 2.6 Operating parameters should be set as specified by the particular instrument manufacturer.

3.0 Notes

- 3.1 The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
- 3.2 The use of background correction is required.
- 3.3 The use of halide acids should be avoided.
- 3.4 If absorption to container walls or formation of AgCl is suspected, see Exhibit D, Part C, Atomic Absorption Methods, Flame Technique.
- 3.5 For every sample analyzed, verification is necessary to determine that method of standard additions is not required (see Exhibit E).
- 3.6 If method of standard additions is required, follow the procedure given in Exhibit E.

*REAP-M modified for the Regional Environmental Analytical Procurement.

THALLIUM

Method 279.2 REAP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

1.0 Preparation of Standard Solution

- 1.1 Stock solution: Dissolve 1.303 g of thallium nitrate, $TlNO_3$ (analytical reagent grade) in deionized distilled water. Add 10 mL of concentrated nitric acid and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Tl (1000 mg/L).
- 1.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for method of standard additions.
- 1.3 The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

2.0 Instrument Parameters (General)

- 2.1 Drying Time and Temp: 30 sec @ 125°C.
- 2.2 Ashing Time and Temp: 30 sec @ 400°C.
- 2.3 Atomizing Time and Temp: 10 sec @ 2400°C.
- 2.4 Purge Gas Atmosphere: Argon
- 2.5 Wavelength: 276.8 nm
- 2.6 Operating parameters should be set as specified by the particular instrument manufacturer.

3.0 Notes

- 3.1 The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
- 3.2 The use of background correction is required.
- 3.3 Nitrogen may also be used as the purge gas.
- 3.4 For every sample analyzed, verification is necessary to determine that method of standard additions is not required (see Exhibit E).
- 3.5 If method of standard additions is required, follow the procedure given in Exhibit E.

*REAP-M modified for the Regional Environmental Analytical Procurement.

PART C - ATOMIC ABSORPTION METHODS, FLAME TECHNIQUE⁺

Table of Contents

Analyte/Method

Page No.

Calcium - Method 215.1 REAP-M*	D-55
Magnesium - Method 242.1 REAP-M	D-56
Potassium - Method 258.1 REAP-M	D-57
Sodium - Method 273.1 REAP-M	D-58

⁺From "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA EMSL, Cincinnati, Ohio, August 1977, Revised October 1980, as modified for use in the Regional Environmental Analytical Procurement.

*REAP-M modified for the Regional Environmental Analytical Procurement.

CALCIUM

Method 215.1 REAP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.2-7 mg/L using a wavelength of 422.7 nm

Sensitivity: 0.08 mg/L

Detection Limit: 0.01 mg/L

1.0 Preparation of Standard Solution

- 1.1 Stock Solution: Suspend 1.250 g of CaCO_3 (analytical reagent grade), dried at 180°C for 1 hour before weighing, in deionized distilled water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1000 mL with deionized distilled water. 1 mL = 0.5 mg Ca (500 mg/L).
- 1.2 Lanthanum chloride solution: Dissolve 29 g of La_2O_3 , slowly and in small portions, in 250 mL concentrated HCl (Caution: Reaction is violent) and dilute to 500 mL with deionized distilled water.
- 1.3 Prepare dilutions of the stock calcium solution to be used as calibration standards at the time of analysis. To each 10 mL of calibration standard and sample alike add 1.0 mL of the lanthanum chloride solution, i.e., 20 mL of standard or sample + 2 mL LaCl_3 = 22 mL.

2.0 Instrumental Parameters (General)

- 2.1 Calcium hollow cathode lamp
- 2.2 Wavelength: 422.7 nm
- 2.3 Fuel: Acetylene
- 2.4 Oxidant: Air
- 2.5 Type of flame: Reducing

3.0 Notes

- 3.1 Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Because low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1000 mg/L also cause low calcium values. Concentrations of up to 500 mg/L each of sodium, potassium and nitrate cause no interference.
- 3.2 Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.
- 3.3 The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame. (Atomic Absorption Newsletter 14, 29 [1975])
- 3.4 The 239.9 nm line may also be used. This line has a relative sensitivity of 120.

*REAP-M modified for the Regional Environmental Analytical Procurement.

MAGNESIUM

Method 242.1 REAP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.02-0.5 mg/L using a wavelength of 285.2 nm

Sensitivity: 0.007 mg/L

Detection Limit: 0.001 mg/L

1.0 Preparation of Standard Solution

- 1.1 Stock Solution: Dissolve 0.829 g of magnesium oxide, MgO (analytical reagent grade), in 10 mL of redistilled HNO₃ and dilute to 1 liter with deionized distilled water. 1 mL = 0.50 mg Mg (500 mg/L).
- 1.2 Lanthanum chloride solution: Dissolve 29 g of La₂O₃, slowly and in small portions in 250 mL concentrated HCl (Caution: Reaction is violent), and dilute to 500 mL with deionized distilled water.
- 1.3 Prepare dilutions of the stock magnesium solution to be used as calibration standards at the time of analysis. To each 10 mL volume of calibration standard and sample alike add 1.0 mL of the lanthanum chloride solution, i.e., 20 mL of standard or sample + 2 mL LaCl₃ = 22 mL.

2.0 Instrumental Parameters (General)

- 2.1 Magnesium hollow cathode lamp
- 2.2 Wavelength: 285.2 nm
- 2.3 Fuel: Acetylene
- 2.4 Oxidant: Air
- 2.5 Type of flame: Oxidizing

3.0 Notes

- 3.1 The interference caused by aluminum at concentrations greater than 2 mg/L is masked by addition of lanthanum. Sodium, potassium and calcium cause no interference at concentrations less than 400 mg/L.
- 3.2 The 202.5nm line may also be used. This line has a relative sensitivity of 25.
- 3.3 To cover the range of magnesium values normally observed in surface waters (0.1-20 mg/L), it is suggested that either the 202.5 nm line be used or the burner head be rotated. A 90° rotation of the burner head will produce approximately one-eighth the normal sensitivity.

*REAP-M modified for the Regional Environmental Analytical Procurement.

POTASSIUM

Method 258.1 REAP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.1-2 mg/L using a wavelength of 766.5 nm

Sensitivity: 0.04 mg/L

Detection Limit: 0.01 mg/L

1.0 Preparation of Standard Solution

- 1.1 Stock Solution: Dissolve 0.1907 g of KCl (analytical reagent grade), dried at 110°C, in deionized distilled water and make up to 1 liter. 1 mL = 0.10 mg K (100 mg/L).
- 1.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

2.0 Instrumental Parameters (General)

- 2.1 Potassium hollow cathode lamp
- 2.2 Wavelength: 766.5 nm
- 2.3 Fuel: Acetylene
- 2.4 Oxidant: Air
- 2.5 Type of flame: Slightly oxidizing

3.0 Notes

- 3.1 In air-acetylene or other high temperature flames (>2800°C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1000 ug/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks must be analyzed to correct for potassium impurities in the buffer zone.
- 3.2 The 404.4 nm line may also be used. This line has a relative sensitivity of 500.
- 3.3 To cover the range of potassium values normally observed in surface waters (0.1-20 mg/L), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides approximately one-eighth the normal sensitivity.

*REAP-M modified for the Regional Environmental Analytical Procurement.

SODIUM

Method 273.1 REAP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.03-1 mg/L using a wavelength of 589.6 nm

Sensitivity: 0.015 mg/L

Detection Limit: 0.002 mg/L

1.0 Preparation of Standard Solutions

- 1.1 Stock Solution: Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in deionized distilled water and make up to 1 liter. 1 mL = 1 mg Na (1000 mg/L).
- 1.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

2.0 Instrumental Parameters (General)

- 2.1 Sodium hollow cathode lamp
- 2.2 Wavelength: 589.6 nm
- 2.3 Fuel: Acetylene
- 2.4 Oxidant: Air
- 2.5 Type of flame: Oxidizing

3.0 Notes

- 3.1 The 330.2 nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.
- 3.2 Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1000 mg/L) to both standards and samples.

*REAP-M modified for the Regional Environmental Analytical Procurement.

Exhibit D -- Section IV
Part C - Flame AA

PART D - COLD VAPOR METHODS FOR MERCURY ANALYSIS

Table of Contents

<u>Method</u>	<u>Page No.</u>
Mercury Analysis in Aqueous Samples (Medium and Low Level) by Manual Cold Vapor Technique, Method 245.1 REAP-M*	D-60
Mercury Analysis in Aqueous Samples (Medium and Low Level) by Automated Cold Vapor Technique, Method 245.2 REAP-M	D-65
Mercury Analysis in Soil/Sediment/Solid Samples by Manual Cold Vapor Technique, Method 245.5 REAP-M	D-68

*REAP-M modified for the Regional Environmental Analytical Procurement.

**MERCURY ANALYSIS IN AQUEOUS SAMPLES (MEDIUM AND LOW LEVEL)
BY MANUAL COLD VAPOR TECHNIQUE**

MERCURY
Method 245.1 REAP-M* (Manual Cold Vapor Technique)

1.0 Scope and Application

- 1.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to ensure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in, or spiked to, a natural system.
- 1.2 This method is applicable to the analysis of mercury in Medium and Low Level aqueous samples. Detection limits vary depending on the instrument configuration and selected operating conditions. The range of the method may be varied through instrument and/or recorder expansion.
- 1.3 If additional sensitivity is required, then a larger sample volume, up to 200 mL, with recorder expansion may be used provided that the instrument does not produce undue noise. The Contractor must achieve and demonstrate a steady baseline and meet all QA/QC requirements as specified in Exhibit E. The method detection limit study, as specified in Exhibit E, must be performed under the same conditions used for sample preparation and analysis.

2.0 Summary of Method

- 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of micrograms of mercury.
- 2.2 A 100 mL sample volume is used for Medium and Low Level aqueous samples. If the Contractor cannot achieve the Low Level CRQL using a 100 mL sample volume, then a 200 mL sample volume with recorder expansion may be used to achieve the Low Level CRQL requirements. However, all reagents must be added to the sample proportionately.

3.0 Sample Handling and Preservation

- 3.1 Samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection (Exhibit D, Section II).

*REAP-M modified for the Regional Environmental Analytical Procurement.

4.0 Interference

- 4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water (Exhibit D, Section II).
- 4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.
- 4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation at 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.

5.0 Apparatus

- 5.1 Atomic absorption spectrophotometer: (See Note 1.) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Follow the instrument settings recommended by the particular manufacturer.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

- 5.2 Mercury hollow cathode lamp: Westinghouse WL-22847, argon filled, or equivalent.
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to find the maximum transmittance.
- 5.5 Air pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.
- 5.7 Aeration tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.
- 5.8 Drying tube: A 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2).

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6.0 Reagents

6.1 Sulfuric acid, concentrated: Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

6.2 Nitric acid, concentrated: Reagent grade of low mercury content (see Note 3).

NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid or use a higher purity acid.

6.3 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.4 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.5 Potassium permanganate (KMnO_4), 5% (w/v) solution: Dissolve 5 g of potassium permanganate in 100 mL of distilled water.

6.6 Potassium persulfate, 5% (w/v) solution: Dissolve 5 g of potassium persulfate in 100 mL of distilled water.

6.7 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL. (1 mL = 1 mg Hg.)

6.8 Working mercury solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7.0 Calibration Procedure

7.1 Prepare a minimum of five standards and a blank by pipetting suitable volumes of the working mercury standard solution (Section 6.8) to a series of 300 mL BOD bottles. NOTE: One calibration standard must be at the CRQL in the sample.

7.1.1 For Medium Level waters: Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury solution containing 0, 0.02, 0.05, 0.1, 0.5, and 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 mL.

7.1.2 For Low Level waters: Transfer 0, 0.1, 0.5, 1.0, 5.0, and 10.0 mL aliquots of the working mercury solution containing 0, 0.01, 0.05, 0.1, 0.5, and 1.0 ug mercury to a series of 300 mL bottles. Add enough distilled water to each bottle to make a total volume of 100 mL. (If a sample volume larger than 100 mL but no greater than 200 mL is used, then the appropriate aliquot volumes must be added.)

7.2 Mix thoroughly and add 5 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid to each bottle. Add 15 mL of 5% (w/v) KMnO_4 (Section 6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 mL of 5% (w/v) potassium persulfate (Section 6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Alternatively, cover the BOD bottles with foil and heat in an autoclave for 15 minutes at 120°C and 15 PSI. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 mL of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation.

7.3 The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (see Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as equal volumes of 0.1 M KMnO_4 , and 10% H_2SO_4 or 0.25% iodine in a 3% a KI solution. A specially treated charcoal that will adsorb mercury vapor is commercially available.

- 7.4 Proceed with the standards and perform a linear regression of standard absorbance (or peak height) vs. micrograms of mercury.

8.0 Sample Analysis Procedure

- 8.1 Transfer 100 mL, or an aliquot diluted to 100 mL (see Note 6), to a 300 mL BOD bottle. (If a larger sample volume is used, but no greater than 200 mL, then all reagents must be added to the sample proportionately.)

NOTE 6: All samples must initially be analyzed undiluted. When the mercury concentration exceeds the highest calibration standard, appropriate dilution, i.e., an aliquot diluted to volume (but not below the CRQL), and reanalysis of the sample are required.

- 8.2 Add 5 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid mixing after each addition. Add 15 mL of 5% (w/v) potassium permanganate solution (Section 6.5) to each sample bottle (see Note 7). For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL of 5% (w/v) potassium persulfate (Section 6.6) to each bottle and heat for 2 hours in a water bath at 95°C.

NOTE 7: The same amount of KMnO_4 added to the samples should be present in standards and blanks.

- 8.3 Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate (see Note 8). Purge the headspace in the BOD bottle for at least 1 minute and add 5 mL of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described in Section 7.4 under Calibration Procedure.

NOTE 8: Add reductant in 6 mL increments until KMnO_4 is completely reduced.

9.0 Calculations

- 9.1 Using the absorbance (or peak height) of the analytical sample, determine the micrograms of mercury in that sample using the linear regression equation from the calibration.
- 9.2 Calculate the mercury concentration in the sample using Equation 1:

EQ. 1,

$$\text{ug Hg/L} = \frac{\text{ug Hg, curve}}{\text{aliquot volume, mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

10.0 Quality Control

Quality control shall be performed as specified in Exhibit E.

11.0 Appendix

- 11.1 If additional sensitivity is required, a 200 mL sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, and a 200 mL sample volume for additional sensitivity, a 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 ug/L, the standard deviations were ± 0.027 , ± 0.0006 , ± 0.01 and ± 0.004 . Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.
- 11.2 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water," p. 349, Method D3223 (1976).

**MERCURY ANALYSIS IN AQUEOUS SAMPLES (MEDIUM AND LOW LEVEL)
BY AUTOMATED COLD VAPOR TECHNIQUE**

MERCURY
Method 245.2 REAP-M* (Automated Cold Vapor Technique)

1.0 Scope and Application

- 1.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, an automated persulfate oxidation step following the automated addition of the permanganate has been included to ensure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.
- 1.2 This method is applicable to the analysis of mercury in Medium and Low Level aqueous samples. Detection limits vary depending on the instrument configuration and selected operating conditions. If the Low Level CRQL requirements cannot be achieved using this method, then the Contractor must use the manual cold vapor technique.

2.0 Summary of Method

- 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

3.0 Sample Handling and Preservation

- 3.1 Samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection (Exhibit D, Section II).

4.0 Interferences (see NOTE 1)

- 4.1 Some sea waters and waste-waters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.
- 4.2 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.
- 4.3 Samples containing solids must be blended and then mixed while being sampled if total mercury values are to be reported.

NOTE 1: All of the above interferences can be overcome by use of the Manual Mercury method.

*REAP-M modified for the Regional Environmental Analytical Procurement.

5.0 Apparatus

5.1 Technicon Auto Analyzer or equivalent instrumentation consisting of:

5.1.1 Sampler II with provision for sample mixing.

5.1.2 Manifold.

5.1.3 Proportioning Pump II or III.

5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116-0163) in series.

5.2 Vapor-liquid separator.

5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.

5.4 Atomic absorption spectrophotometer (see Note 2): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 2: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.5 Mercury hollow cathode lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

6.0 Reagents

6.1 Sulfuric Acid, concentrated: Reagent grade

6.1.1 Sulfuric acid, 2 N: Dilute 56 mL of concentrated sulfuric acid to 1 liter with distilled water.

6.1.2 Sulfuric acid, 10% (v/v): Dilute 100 mL concentrated sulfuric acid to 1 liter with distilled water.

6.2 Nitric acid, concentrated: Reagent grade of low mercury content.

6.2.1 Nitric Acid, 0.5% (v/v) wash solution: Dilute 5 mL of concentrated nitric acid to 1 liter with distilled water.

6.3 Stannous Sulfate (See Note 3): Add 50 g stannous sulfate to 500 mL of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.

NOTE 3: Stannous chloride may be used in place of stannous sulfate.

6.4 Sodium chloride-hydroxylamine sulfate (See Note 4) Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.

NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

6.5 Potassium permanganate (KMnO_4), 0.5% (w/v) solution: Dissolve 5 g of potassium permanganate in 1 liter of distilled water.

6.6 Potassium permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.

- 6.7 Potassium persulfate, 0.5% (w/v) solution: Dissolve 5 g of potassium persulfate in 1 liter of distilled water.
- 6.8 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL. 1.0 mL = 1.0 mg Hg.
- 6.9 Working mercury solution: Make successive dilutions of the stock mercury solution (Section 6.8) to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution, prepare standards containing mercury in the following recommended concentrations: 0.1 or 0.2 (depending on the CRQL level), 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 ug Hg/L.
- 6.10 Air scrubber solution: Mix equal volumes of 0.1 N potassium permanganate (Section 6.6) and 10% sulfuric acid (Section 6.1.2).
- 7.0 Procedure (See Note 5)
- 7.1 Set up the manifold as recommended by the manufacturer.
- 7.2 Feeding all the reagents through the system with acid wash solution (Section 6.2.1) through the sample line. Adjust the heating bath to 105°C.
- 7.3 Turn on the atomic absorption spectrophotometer and adjust instrument settings as recommended by the manufacturer. Align the absorption cell in the light path for maximum transmittance and place the heat lamp directly over the absorption cell.
- 7.4 Arrange working mercury standards from 0 to 20.0 ug Hg/L in the sampler and start sampling. NOTE: One calibration standard must be at the CRQL in the sample. Complete loading the sample tray with samples.
- 7.5 After the analysis is complete, put all lines except the H₂SO₄ line in distilled water to wash out system. After flushing, wash out the H₂SO₄ line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (Section 6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as equal volumes of 0.1 N KMnO₄ (Section 6.6) and 10% H₂SO₄ (Section 6.1.2), or 0.25% iodine in a 3% KI solution, is recommended. A specially treated charcoal that will absorb mercury vapor is also available.

- 8.0 Calculations
- 8.1 Perform a linear regression of standard absorbance (or peak height) vs. µg of Hg/L. Use the linear regression equation to determine the concentration of mercury in field and QC samples.
- 8.2 If samples were diluted for analysis, multiply the results obtained from the linear regression by the dilution factor.
- 9.0 Quality Control
- Quality control shall be performed as specified in Exhibit E.

**MERCURY ANALYSIS IN SOIL/SEDIMENT/SOLID SAMPLES
BY MANUAL COLD VAPOR TECHNIQUE**

MERCURY
Method 245.5 REAP-M* (Manual Cold Vapor Technique)

1.0 Scope and Application

- 1.1 This procedure measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge type materials.
- 1.2 The range of the method is 0.1 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.

2.0 Summary of Method

- 2.1 A weighed portion of the sample is acid digested for 2 minutes at 95°C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique.
- 2.2 An alternate digestion involving the use of an autoclave is described in Section 8.2.

3.0 Sample Handling and Preservation

- 3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.
- 3.2 Refrigerate solid samples at 4°C (±2°) upon receipt until analysis (see Exhibit D, Section II).
- 3.3 The sample should be analyzed without drying. A separate percent solids determination is required (Part F).

4.0 Interferences

- 4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.
- 4.2 Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

*REAP-M modified for the Regional Environmental Analytical Procurement.

5.0 Apparatus

- 5.1 Atomic absorption spectrophotometer (see Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

- 5.2 Mercury hollow cathode lamp: Westinghouse WL-22847, argon filled, or equivalent.
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption cell: Standard spectrophotometer cells 10 cm long, having quartz end windows, may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance. Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.
- 5.5 Air pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.
- 5.7 Aeration tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.
- 5.8 Drying tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2).

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6.0 Reagents

- 6.1 Sulfuric acid, concentrated: Reagent grade of low mercury content.
- 6.2 Nitric acid, concentrated: Reagent grade of low mercury content.
- 6.3 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid (6.1). This mixture is a suspension and should be stirred continuously during use.
- 6.4 Sodium chloride-hydroxylamine sulfate (See Note 3) solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL.
- NOTE 3: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).
- 6.5 Potassium permanganate (KMnO_4), 5% (w/v) solution: Dissolve 5 g of potassium permanganate in 100 mL of distilled water
- 6.6 Potassium persulfate, 5% (w/v) solution: Dissolve 5 g of potassium persulfate in 100 mL of distilled water.
- 6.7 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL. 1.0 = 1.0 mg Hg.
- 6.8 Working mercury solution: Make successive dilutions of the stock mercury solution (6.7) to obtain a working standard containing 0.1 ug/mL. This

working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7.0 Calibration Procedure

- 7.1 Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10 mL aliquots of the working mercury solutions (Section 6.8) containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 mL. Add 5 mL of concentrated H_2SO_4 (Section 6.1) and 2.5 mL of concentrated HNO_3 (Section 6.2) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 mL distilled water, 15 mL of $KMnO_4$ solution (Section 6.5) and 8 mL of potassium persulfate solution (6.6) to each bottle and return to the water bath for 30 minutes.
- 7.2 Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (Section 6.4) to reduce the excess permanganate. Add 50 mL of distilled water (final volume of distilled water = 100 mL). Treating each bottle individually, add 5 mL of stannous sulfate solution (Section 6.3) and immediately attach the bottle to the aeration apparatus. At this point the sample is allowed to stand quietly without manual agitation.
- 7.3 The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 4). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration.

NOTE 4: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as: a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4 , or b) 0.25% iodine in a 3% KI solution. A specially treated charcoal that will absorb mercury vapor is also commercially available.

- 7.4 Proceed with the standards and perform a linear regression a standard curve by plotting peak height versus micrograms of mercury. Use the linear regression equation to determine the amount of mercury in field and QC samples.

8.0 Analysis Procedure

Prior to sample digestion, the percent solids of the soil/sediment sample must be determined in accordance with Section IV, Part F and the appropriate procedures must be followed for percent solids less than or equal to 30%.

- 8.1 Weigh a representative 0.2 g portion of wet sample and place in the bottom of a BOD bottle (see Note 5). Add enough distilled water to each sample to make a total volume of 10 mL. Add 5 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid mixing after each addition. Heat two minutes in a water bath at 95°C. Cool, add 50 mL distilled water, 15 mL potassium permanganate solution (Section 6.5) and 8 mL of potassium persulfate solution (Section 6.6) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (Section 6.4) to reduce the excess permanganate. Add 50 mL of distilled water (final volume of distilled water = 100 mL). Treating each bottle individually, purge the head space of the sample bottle for at least one minute and add 5 mL of stannous sulfate (Section 6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Section 7.1.

NOTE 5: All samples must initially be analyzed undiluted (i.e., 0.2 g sample amount). When the mercury concentration exceeds the highest calibration standard, a portion of sample less than 0.2 g and reanalysis are required to bring the concentration within the linear range (but not below the CRQL).

- 8.2 An alternate digestion procedure employing an autoclave may also be used. In this method add 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 to the 0.2 g of sample. Add 5 mL of saturated $KMnO_4$ solution and 8 mL of potassium persulfate solution and cover the bottle with a piece of aluminum foil. Autoclave the sample at 121°C and 15 PSI for 15 minutes. Cool, make up to a volume of 100 mL with distilled water and add 6 mL of sodium chloride-hydroxylamine sulfate solution (Section 6.4) to reduce the excess

permanganate. Purge the headspace of the sample bottle for at least one minute and continue as described under 7.1.

9.0 Calculations

9.1 Using the absorbance (or peak height) of the analytical sample, determine the micrograms of mercury in that sample using the linear regression equation from the calibration.

9.2 Calculate the mercury concentration in the sample using Equation 1:

EQ. 1,

$$\mu\text{g Hg/g} = \frac{\mu\text{g/L Hg, curve}}{\text{aliquot dry wt., g}} \times \text{final vol. after prep., L}$$

9.3 Report mercury concentrations as described in Exhibit B. The sample result or the method detection limit for each sample must be corrected for sample weight and % solids before reporting.

NOTE 6: $\mu\text{g/g}$ is equivalent to mg/kg .

10.0 Quality Control

Quality control shall be performed as specified in Exhibit E.

PART E - METHODS FOR TOTAL CYANIDE ANALYSIS

Table of Contents

<u>Method</u>	<u>Page No.</u>
Method for Total Cyanide Analysis in Aqueous Samples (Medium and Low Level), Method 335.2 REAP-M*	D-73
Method for Total Cyanide Analysis in Soil/Sediment/Solid Samples, Method 335.2 REAP-M	D-79
Method for Total Cyanide Analysis in Aqueous (Medium and Low Level) and Soil/Sediment/Solid Samples by Midi Distillation, Method 335.2 REAP-M	D-85

*REAP-M Modified for the Regional Environmental Analytical Procurement.

METHOD FOR TOTAL CYANIDE ANALYSIS IN AQUEOUS SAMPLES (MEDIUM AND LOW LEVEL)

CYANIDE, TOTAL

Method 335.2 REAP-M*
(Manual Spectrophotometric; Semi-Automated Spectrophotometric)

1.0 Scope and Application

- 1.1 This method is applicable to the determination of cyanide in drinking, surface and saline waters, and domestic and industrial wastes.
- 1.2 The applicable range is approximately 5 µg/L to 500 µg/L.

2.0 Summary of Method

- 2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.
- 2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

3.0 Definitions

- 3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4.0 Sample Handling and Preservation

- 4.1 All bottles must be thoroughly cleansed and rinsed to remove soluble material from containers.
- 4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.
- 4.3 Samples are preserved with 2 mL of 10 N sodium hydroxide per liter of sample (pH > 12) at the time of collection (Exhibit D, Section II).
- 4.4 Samples must be stored at 4°C(±2°C) and must be analyzed within the holding time specified in Exhibit D, Section II.

5.0 Interferences

- 5.1 Interferences are eliminated or reduced by using the distillation procedure described in 8.1.

*REAP-M Modified for the Regional Environmental Analytical Procurement.

- 5.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the distillate on lead acetate test paper indicates the presence of sulfides, treat 25 mL more of the sample than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. Sulfides should be removed prior to preservation with sodium hydroxide as described in 4.3.
- 5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.
- 6.0 Apparatus
- 6.1 Reflux distillation apparatus: A 1 liter boiling flask with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.
- 6.2 Microburet, 5.0 mL (for titration)
- 6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger (for manual spectrophotometric method).
- 6.4 Technicon AA II system or equivalent instrumentation (for automated spectrophotometric method) including:
- 6.4.1 Sampler
- 6.4.2 Pump III
- 6.4.3 Cyanide manifold
- 6.4.4 SCIC colorimeter with 15 mm flowcells and 570 nm filters
- 6.4.5 Recorder
- 6.4.6 Data system (optional)
- 6.4.7 Glass or plastic tubes for the sampler
- 7.0 Reagents
- 7.1 Distillation and Preparation Reagents
- 7.1.1 Sodium hydroxide solution, 1.25 N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.
- 7.1.2 Cadmium carbonate: powdered
- 7.1.3 Ascorbic acid: crystals
- 7.1.4 Sulfuric acid: concentrated
- 7.1.5 Magnesium chloride solution: Weigh 510 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ into a 1000 mL flask, dissolve, and dilute to 1 liter with distilled water.

Exhibit D -- Section IV
Part E - Cyanide

7.2 Stock Standards and Titration Reagents

- 7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N AgNO₃.
- 7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 mL of stock (1 mL = 1 mg CN) to 1000 mL with distilled water.
- 7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass stoppered bottle. 1 mL = 5.0 ug CN (5.0 mg/L).
- 7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g AgNO₃ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried AgNO₃, dissolve in distilled water, and dilute to 1000 mL (1 mL = 1 mg CN).
- 7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-aminobenzalrhodanine in 100 mL of acetone.
- 7.2.6 Sodium hydroxide solution, 0.25 N: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

7.3 Manual Spectrophotometric Reagents

- 7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of NaH₂PO₄•H₂O in a liter of distilled water. Refrigerate this solution.
- 7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.
- 7.3.3 Color Reagent-One of the following may be used:
- 7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.
- 7.3.3.2 Pyridine-pyrazolone solution:
- 7.3.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, heat to 60°C with stirring. Cool to room temperature.
- 7.3.3.2.2 3,3'-Dimethyl-1,1'-diphenyl [4,4'-bis-2-pyrazolin]-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.
- 7.3.3.2.3 Pour solution (Section 7.3.3.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (Section 7.3.3.2.2) collecting the filtrate in the same container as filtrate from (Section 7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

- 7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 mL. Prepare fresh daily.
- 7.4.2 Phosphate buffer: Dissolve 138 g of NaH₂PO₄•H₂O in distilled water and dilute to 1 liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at 4°C(±2°C).
- 7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 mL of distilled water and swirl the flask. Add 74 mL of pyridine and mix. Add 15 mL of concentrated HCl and mix. Dilute to about 900 mL with distilled water and mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at 4°C(±2°C).

7.4.4 Sampler wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8.0 Procedure

8.1 Distillation

8.1.1 Place 500 mL of sample in the 1 liter boiling flask. Add 50 mL of 1.25 N sodium hydroxide to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

8.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.1.3 Slowly add 25 mL concentrated sulfuric acid (Section 7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (Section 7.1.5) into the air inlet and wash down with a stream of water.

8.1.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.1.5 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with distilled water washings from the absorber tube.

NOTE: The distillation procedure results in a 2x concentration of the sample.

8.2 Manual Spectrophotometric Determination (Option A)

8.2.1 Withdraw 50 mL, or less (see Note 1), of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution (Section 7.2.6). Add 15.0 mL of sodium phosphate solution (Section 7.3.1) and mix. The dilution factor must be reported on Form XIV.

NOTE 1: All samples must initially be analyzed undiluted. When the cyanide concentration exceeds the highest calibration standard, an aliquot less than 50 mL shall be taken and reanalysis of the sample is required (but not below the CRQL). The dilution factor must be reported on Form 14.

8.2.1.1 Pyridine-barbituric acid method: Add 2 mL of chloramine-T (Section 7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (Section 7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.2.1.2 Pyridine-pyrazolone method: Add 0.5 mL of chloramine-T (Section 7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-pyrazolone solution (Section 7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes, read absorbance at 620 nm in a 1 cm cell.
NOTE: More than 0.5 mL of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.2.2 Prepare a minimum of 5 standards and a blank by pipetting suitable volumes of standard solution into 250 mL volumetric flasks. NOTE: One calibration standard must be at the Contract Required Quantitation Limit (CRQL). To each standard, add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with distilled water. The same method for color development (i.e., pyridine-barbituric acid or pyridine-pyrazolone) must be used for both the samples and standards. Standards must bracket the concentration of the samples. If dilution is required, use the blank solution.

As an example, standard solutions could be prepared as follows:

mL of Standard Solution	Conc. ug CN
<u>(1.0 = 5 ug CN)</u>	<u>per 250 mL</u>

Exhibit D -- Section IV
Part E - Cyanide

0	Blank
0.5	2.5
1.0	5
5.0	25
10.0	50
15.0	75
20.0	100

- 8.2.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If the distilled standard does not agree within $\pm 15\%$ of the undistilled standards, the operator should find and correct the cause of the apparent error before proceeding. All samples, field and QC samples distilled with the noncompliant standard must be redistilled.
- 8.2.2.2 Perform a linear regression of absorbance of standard vs. cyanide concentrations (per 250 mL).
- 8.3 Semi-Automated Spectrophotometric Determination (Option B)
- 8.3.1 Set up the manifold. Pump the reagents through the system until a steady baseline is obtained.
- 8.3.2 Calibration standards: Prepare a blank and at least five calibration standards over the range of the analysis. One calibration standard must be at the CRQL. For a working range of 0-200 ug/L, the following standards may be used:

<u>mL Standard Solution (7.2.3) diluted to 1 liter</u>	<u>Concentration ug CN/L</u>
0	0
2.0	10
4.0	20
10.0	50
20.0	100
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C(±2°C)

- 8.3.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.
- 8.3.4 When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL dial on the colorimeter until the desired signal is obtained. Record the STD CAL value. Re-establish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

9.0 Calculations

- 9.1 If the manual spectrophotometric procedure is used, calculate the cyanide, in ug/L, in the original sample using Equation 1:

EQ. 1,

$$CN, (\mu g/L) = \frac{A \times 1000 \text{ mL/L}}{B} \times \frac{50 \text{ mL}}{C}$$

where,

A = ug CN read from standard curve (per 250 mL)
 B = mL of original sample for distillation (See Section 8.1.1)
 C = mL taken for colorimetric analysis (See Section 8.3.1)

50 mL = volume of original sample aliquot (See Section 8.3.1)
 1000 mL/L = conversion mL to L

- 9.2 If the semi-automated method is used, measure the absorbance (or peak height) of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the field samples and QC samples to determine the cyanide concentration in the distillates. To determine the concentration of cyanide in the original sample, MULTIPLY THE RESULTS BY ONE-HALF (since the original volume was 500 mL and the distillate volume was 250 mL). Also, correct for, and report on Form XIV, any dilutions which were made before or after distillation.

10.0 Quality Control

Quality control shall be performed as specified in Exhibit E.

METHOD FOR TOTAL CYANIDE ANALYSIS IN SOIL/SEDIMENT/SOLID SAMPLES

CYANIDE, TOTAL

Method 335.2 REAP-M*
(Manual Spectrophotometric; Semi-Automated Spectrophotometric)

1.0 Scope and Application

- 1.1 This method is applicable to the determination of cyanide in sediments and other solids.
- 1.2 The detection limit is dependent upon the weight of sample taken for analysis.

2.0 Summary of Method

- 2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.
- 2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CNCl , by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone for 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

3.0 Definitions

- 3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4.0 Sample Handling and Preservation

- 4.1 Samples must be stored at $4^{\circ}\text{C}(\pm 2^{\circ}\text{C})$ and must be analyzed within the holding time specified in Exhibit D, Section II.
- 4.2 Samples are not dried prior to analysis. A separate percent solids determination must be made in accordance with the procedure in Part F.

5.0 Interferences

- 5.1 Interferences are eliminated or reduced by using the distillation procedure described in 8.1.
- 5.2 Sulfides adversely affect the colorimetric procedures.
- 5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as DOW Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

*REAP-M Modified for the Regional Environmental Analytical Procurement.

6.0 Apparatus

- 6.1 Reflux distillation apparatus: A 1 liter boiling flask with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.
- 6.2 Microburet, 5.0 mL (for titration)
- 6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.
- 6.4 Technicon AA II system or equivalent instrumentation (for automated spectrophotometric method) including:
 - 6.4.1 Sampler
 - 6.4.2 Pump III
 - 6.4.3 Cyanide manifold
 - 6.4.4 SCIC colorimeter with 15 mm flowcells and 570 nm filters
 - 6.4.5 Recorder
 - 6.4.6 Data system (optional)
 - 6.4.7 Glass or plastic tubes for the sampler

7.0 Reagents

7.1 Distillation and Preparation Reagents

- 7.1.1 Sodium hydroxide solution, 1.25 N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.
- 7.1.2 Cadmium carbonate: powdered
- 7.1.3 Ascorbic acid: crystals
- 7.1.4 Sulfuric acid: concentrated
- 7.1.5 Magnesium chloride solution: Weigh 510 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ into a 1000 mL flask, dissolve and dilute to 1 liter with distilled water.

7.2 Stock Standards and Titration Reagents

- 7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g of KOH in 1 liter of distilled water. Standardize with 0.0192 N AgNO_3 .
- 7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 mL of stock (1 mL = 1 mg CN) to 1000 mL with distilled water (1 mL = 50.0 ug).
- 7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass stoppered bottle. 1 mL = 5.0 ug CN (5.0 mg/L).
- 7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g AgNO_3 crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried AgNO_3 , dissolve in distilled water, and dilute to 1000 mL (1 mL = 1 mg CN).
- 7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 mL acetone.

Exhibit D -- Section IV
Part E - Cyanide

7.3 Manual Spectrophotometric Reagents

- 7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 1 liter of distilled water. Refrigerate this solution.
- 7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble Chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.
- 7.3.3 Color reagent - One of the following may be used:
- 7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.
- 7.3.3.2 Pyridine-pyrazolone solution:
- 7.3.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, heat to 60°C with stirring. Cool to room temperature.
- 7.3.3.2.2 3,3'-Dimethyl-1,1'-diphenyl-[4,4'-bi-2-pyrazolin]-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.
- 7.3.3.2.3 Pour solution (7.3.3.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.3.3.2.2) collecting the filtrate in the same container as filtrate from (7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

- 7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 mL. Prepare fresh daily.
- 7.4.2 Phosphate Buffer: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in distilled water and dilute to 1 liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at 4°C.
- 7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 mL of distilled water and swirl the flask. Add 74 mL of pyridine and mix. Add 15 mL of conc. HCl mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at 4°C.
- 7.4.4 Sampler Wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8.0 Procedure

8.1 Distillation

Prior to sample distillation, the percent solids of the soil/sediment sample must be determined in accordance with Section IV, Part F and the appropriate procedures must be followed for percent solids less than or equal to 30%.

- 8.1.1 Accurately weigh a representative 1-5 g portion of wet sample and transfer it to a boiling flask. Add 500 mL of distilled water. Shake or stir the sample so that it is dispersed.
- 8.1.2 Add 50 mL of sodium hydroxide (7.1.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the train.
- 8.1.3 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.1.4 Slowly add 25 mL of conc. sulfuric acid (7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (7.1.5) into the air inlet and wash down with a stream of water.

8.1.5 Heat the solution to boiling, taking care to prevent the solution from backing up and overflowing into the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.1.6 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with distilled water washings from the absorber tube.

NOTE: The distillation procedure results in a 2x concentration of the sample.

8.2 Manual Spectrophotometric Determination (Option A)

8.2.1 Withdraw 50 mL, or less (see Note 1), of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution (7.1.1). Add 15.0 mL of sodium phosphate solution (7.3.1) and mix.

NOTE 1: All samples must initially be analyzed undiluted. When the cyanide concentration exceeds the highest calibration standard, an aliquot less than 50 mL shall be taken and reanalysis of the sample is required (but not below the CRQL). The dilution factor must be reported on Form 14.

8.2.1.1 Pyridine-barbituric acid method: Add 2 mL of Chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.2.1.2 Pyridine-pyrazolone method: Add 0.5 mL of chloramine-T (7.3.2) and mix. After 1 to 2 minutes add 5 mL of pyridine-pyrazolone solution (7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes, read absorbance at 620 nm in a 1 cm cell.

NOTE: More than 0.5 mL of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.2.2 Prepare a minimum of five standards and a blank by pipetting suitable volumes of standard solution into 250 mL volumetric flasks. NOTE: One calibration standard must be made at the CRQL. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with distilled water. The same method for color development (i.e., pyridine-barbituric acid or pyridine-pyrazolone) must be used for both the samples and standards. Standards must bracket the concentrations of the sample. If dilution is required, use the blank solution.

As an example, standard solutions could be prepared as follows:

<u>mL of Standard Solution</u> <u>(1.0 = 5 ug CN)</u>	<u>Conc. ug CN</u> <u>per 250 mL</u>
0	Blank
0.5	2.5
1.0	5
5.0	25
10.0	50
15.0	75
20.0	100

8.2.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If the distilled standard does not agree within $\pm 15\%$ of the undistilled standards the operator should find and correct the cause of the apparent error before proceeding.

Exhibit D -- Section IV
Part E - Cyanide

8.2.2.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations (per 250 mL).

8.3 Semi-Automated Spectrophotometric Determination (Option B)

8.3.1 Set up the manifold as recommended by the manufacturer. Pump the reagents through the system until a steady baseline is obtained.

8.3.2 Calibration standards: Prepare a blank and at least five calibration standards over the range of the analysis. One calibration standard must be at the CRQL. For a working range of 0-200 ug/L, the following standards may be used:

<u>mL Standard Solution</u> <u>(7.2.3) diluted to 1 liter</u>	<u>Concentration</u> <u>ug CN/L</u>
0.0	0
2.0	10
4.0	20
10.0	50
20.0	100
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C(±2°C).

8.3.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

8.3.4 When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL dial on the colorimeter until the desired signal is obtained. Record the STD CAL value. Reestablish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

8.3.5 Perform a linear regression

9.0 Calculations

9.1 A separate determination of percent solids must be performed (see Part F).

9.2 The concentration of cyanide in the sample is determined as follows.

9.2.1 For the manual spectrophotometric method use Equation 1:

EQ. 1,

$$CN \text{ (mg/Kg)} = \frac{A \times \frac{50 \text{ mL}}{B}}{C \times \frac{\% \text{ solids}}{100}}$$

Where,

A = ug CN read from standard curve (per 250 mL)

B = mL of distillate taken for colorimetric determination (Section 8.2.1)

C = wet weight of original sample in g (See Section 8.1.1)

and,

50 mL = volume of standard taken for colorimetric determination
(See Section 8.2.1)

% solids (see Part F)

9.2.3 If the semi-automated spectrophotometric method is used, measure the absorbance (peak height) of the calibration standards (using a data system or visually) and calculate a linear regression equation. Apply the equation to the field samples and QC samples to determine the cyanide concentration in the distillates. Determine the cyanide concentration in the original sample using Equation 2:

EQ. 2,

$$CN \text{ (mg/Kg)} = \frac{A \times 0.25}{C \times \frac{\% \text{ solids}}{100}}$$

Where,

A = ug/L determined from standard curve

C = wet weight of original sample in g (See 8.1.1)

and,

0.25 = conversion factor for distillate final volume (See 8.1.6)

% solids (see Part F)

10.0 Quality Control

Quality control shall be performed as specified in Exhibit E.

**METHOD FOR TOTAL CYANIDE ANALYSIS OF AQUEOUS (MEDIUM AND LOW LEVEL)
AND SOIL/SEDIMENT/SOLID SAMPLES BY MIDI DISTILLATION**

CYANIDE, TOTAL

Method 335.2 REAP-M* (Semi-automated Spectrophotometric)

1.0 Scope and Application

- 1.1 Cyanide determined by this method is defined as cyanide ion and complex cyanides converted to hydrocyanic acid by reaction in a reflux system with mineral acid in the presence of magnesium ion.
- 1.2 This method covers the determination of cyanide by midi distillation with a semi-automated colorimetric analysis of the distillate.
- 1.3 The applicable range is approximately 5 µg/L to 500 µg/L.

2.0 Summary of Method

- 2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a midi reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.
- 2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at pH less than 8 without hydrolysis to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 580 nm. To obtain colors of comparable intensity, it is essential to have the same salt content in both the samples and the standards.

3.0 Sample Handling and Preservation

- 3.1 All bottles must be thoroughly cleansed and rinsed to remove soluble materials from containers.
- 3.2 Oxidizing agents such as chlorine decompose most cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-Starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add additional 0.6 g of ascorbic acid for each liter of sample volume.
- 3.3 Samples are preserved with 2 mL of 10 N sodium hydroxide per liter of sample (pH > 12) at the time of collection.
- 3.4 Samples must be stored at 4°C(±2°C) and must be analyzed within the holding time specified in Exhibit D, Section II.

4.0 Interferences

- 4.1 Interferences are eliminated or reduced by using the distillation procedure.
- 4.2 Sulfides adversely affect the colorimetric procedures. If a drop of distillate on lead acetate test paper indicates the presence of sulfides, treat the sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material.
- 4.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoaming agent will prevent the foam from collecting in the condenser.

5.0 Apparatus

- 5.1 Midi reflux distillation apparatus.

*REAP-M Modified for the Regional Environmental Analytical Procurement.

- 5.2 Heating block - Capable of maintaining $125^{\circ}\text{C} \pm 5^{\circ}\text{C}$.
- 5.3 Auto analyzer system with accessories:
 - 5.3.1 Sampler
 - 5.3.2 Pump
 - 5.3.3 Cyanide cartridge
 - 5.3.4 Colorimeter with 50 mm flowcells and 580 nm filter
 - 5.3.5 Chart recorder or data system.
- 5.4 Assorted volumetric glassware, pipets, and micropipets.
- 6.0 Reagents
- 6.1 Distillation and Preparation Reagents
 - 6.1.1 Sodium hydroxide absorbing solution and sample wash solution, 0.25 N: Dissolve 10.0 g NaOH in ASTM Type II water and dilute to one liter.
 - 6.1.2 Magnesium chloride solution, 51% (w/v): Dissolve 510 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in ASTM Type II water and dilute to one liter.
 - 6.1.3 Sulfuric acid, 50% (v/v): Carefully add a portion of concentrated H_2SO_4 to an equal portion of ASTM Type II water.
 - 6.1.4 Sodium hydroxide solution, 1.25 N: Dissolve 50 g of NaOH in ASTM Type II water and dilute to one liter.
- 6.2 Standards
 - 6.2.1 Stock cyanide solution, 1000 mg/L CN: Dissolve 2.51 g of KCN and 2.0 g KOH in ASTM Type II water and dilute one liter. Standardize with 0.0192 N AgNO_3 .
 - 6.2.2 Intermediate cyanide standard solution, 10 mg/L CN: Dilute 1.0 mL of stock cyanide solution (Section 6.2.1) plus 20 mL of 1.25 N NaOH solution (Section 6.1.4) to 100 mL with ASTM Type II water. Prepare this solution at time of analysis.
 - 6.2.3 Rhodamine indicator: Dissolve 20 mg of p-dimethylamino-benzal-rhodamine in 100 mL acetone.
 - 6.2.4 Silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g AgNO_3 crystals and drying to a constant weight at 104°C . Weigh out 3.2647 g of dried AgNO_3 and dissolve in ASTM Type II water. Dilute to one liter (1 mL corresponds to 1 mg CN).
 - 6.2.5 Potassium chromate indicator solution: Dissolve 50 g K_2CrO_4 in sufficient ASTM Type II water. Add silver nitrate solution until a definite red precipitate is formed. Let stand for at least 12 hours, filter, and dilute to one liter with ASTM Type II water.
 - 6.2.6 Primary standard sodium chloride, 0.0141 N: Dissolve 824.1 mg NaCl (NBS-dried 20 minutes at 104°C) in ASTM Type II water and dilute to one liter.
 - 6.2.7 Sodium hydroxide solution, 0.1 N: Dissolve 4 g of NaOH in ASTM Type II water and dilute to one liter.
- 6.3 Semi-Automated Spectrophotometric Reagents
 - 6.3.1 Phosphate buffer solution, 1 M: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in ASTM Type II water and dilute to one liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at 4°C .
 - 6.3.2 Chloramine-T solution, 0.4% (w/v): Dissolve 0.4 g of chloramine-T in ASTM Type II water and dilute to 100 mL. Prepare fresh at time of analysis.
 - 6.3.3 Color reagent solution, pyridine barbituric acid color reagent solution: Prepare this solution in the hood. Transfer 15 g of barbituric acid into a one liter Erlenmeyer flask. Add about 100 mL of ASTM Type II water and swirl the flask to mix. Add 75 mL of pyridine and 15 mL concentrated HCl and mix until all the barbituric acid is dissolved. Dilute to one liter with ASTM Type II water and store at 4°C .

Exhibit D -- Section IV
Part E - Cyanide

7.0 Procedure

7.1 Distillation

- 7.1.1 The procedure described here utilizes a midi distillation apparatus and requires a sample aliquot of 50 mL, or less (see Note 1), for aqueous samples and one gram for solid materials.

NOTE 1: All samples must initially be analyzed undiluted (i.e., aqueous samples must first be run with a 50 mL aliquot and solid samples using a one gram sample). When the cyanide concentration exceeds the highest calibration standard, appropriate dilution (but not below the CRQL) and reanalysis of the sample are required. The dilution factor must be reported on Form XIV.

NOTE 2: Prior to sample distillation, the percent solids of the soil/sediment sample must be determined in accordance with Section IV, Part F and the appropriate procedures must be followed for percent solids less than or equal to 30%.

- 7.1.2 For aqueous samples: Pipet 50 mL of sample, or an aliquot diluted to 50 mL, into the distillation flask along with 2 or 3 boiling chips.
- 7.1.3 For solid samples: Weigh 1.0 g of sample (to the nearest 0.01 g) into the distillation flask and dilute to 50 mL with ASTM Type II water. Add 2 or 3 boiling chips.
- 7.1.4 Add 50 mL of 0.25 N NaOH (Section 6.1.1) to the gas absorbing impinger.
- 7.1.5 Connect the boiling flask, condenser, and absorber in the train. The excess cyanide trap contains 0.5 N NaOH.
- 7.1.6 Turn on the vacuum and adjust the gang (Whitney) values to give a flow of three bubbles per second from the impingers in each reaction vessel.
- 7.1.7 After five minutes of vacuum flow, inject 5 mL of 50% (v/v) H_2SO_4 (Section 6.1.3) through the top air inlet tube of the distillation head into the reaction vessel. Allow to mix for 5 minutes. NOTE: The acid volume must be sufficient to bring the sample/solution pH to below 2.0.
- 7.1.8 Add 2 mL of magnesium chloride solution (6.1.2) through the top air inlet tube of the distillation head into the reaction flask. Excessive foaming from samples containing surfactants may be quelled by the addition of another 2 mL of magnesium chloride solution.
- 7.1.9 Turn on the heating block and set for 123-125°C. Heat the solution to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.
- 7.1.10 After one and a half hours of refluxing, turn off the heat and continue the vacuum for an additional 15 minutes. The flasks should be cool at this time.
- 7.1.11 After cooling, close off the vacuum at the gang valve and remove the absorber. Seal the receiving solutions and store them at 4°C until analyzed. The solutions must be analyzed for cyanide within the 12 day holding time specified in Section II.

7.2 Semi-Automated Spectrophotometric Determination

- 7.2.1 Operating conditions: Because of the difference between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. The analyst should follow the instructions provided by the manufacturer of the particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results. The following general procedure applies to most semi-automated colorimeters.
- 7.2.2 Set up the manifold and complete system per manufacturer's instructions. Allow the colorimeter and recorder to warm up for at least 30 minutes prior to use. Establish a steady reagent baseline, feeding ASTM Type II water through the sample line and appropriate reagents (Section 6.3) through reagent lines. Adjust the baseline using the appropriate control on the colorimeter.

- 7.2.3 Prepare a minimum of five standards and a blank by pipetting suitable volumes of standard solution into 50 mL volumetric flasks. NOTE: One calibration standard must be at the Contract Required Quantitation Limit (CRQL).

As an example, standard solutions could be prepared as follows:

<u>Total ug CN standard solution</u>	<u>mL 10 mg/L CN</u>	<u>mL 0.05 N NaOH</u>
0.00	0.000	20
0.10	0.010	20
0.25	0.025	20
0.50	0.050	20
1.00	0.100	20
2.00	0.200	20
5.00	0.500	20
10.00	1.000	20

Exhibit D -- Section IV
Part E - Cyanide

- 7.2.4 Dilute standards to 50 mL using ASTM Type II water. It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve for each SDG to ensure the distillation technique is reliable. If the distilled standard does not agree within $\pm 15\%$ of the undistilled standards, the operator must find and correct the cause of the error before proceeding.
- 7.2.5 Aspirate the highest calibration standard and adjust the colorimeter until the desired (maximum) signal-range is obtained.
- 7.2.6 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.
- 7.2.7 Switch sample line from the ASTM Type II water to sampler, set the appropriate sampling rate and begin the analysis.

8.0 Calculations

8.1 Calculations for Semi-automated Colorimetric Determination

- 8.1.1 Prepare a standard curve by plotting absorbance (peak heights, determined visually or using a data system) of standards (y) versus cyanide concentration values (total ug CN/L) (x). Perform a linear regression analysis.
- 8.1.2 Multiply all distilled values by the standardization value to correct for the stock cyanide solution not being exactly 1000 mg/L (see Section 6.2.1).
- 8.1.3 Using the regression analysis equation, calculate sample receiving solution concentrations from the calibration curve.
- 8.1.4 Calculate the cyanide of aqueous samples in ug/L of original sample using Equation 1:

Equation 1,

$$CN, (\mu g/L) = \frac{A \times D \times F}{B}$$

where,

A = ug/L CN of sample from regression analysis

B = Liter of original sample for distillation (0.050 L) (See 7.1.2)

D = Dilution factor (If no dilution is performed, D = 1)

F = sample receiving solution volume (0.050 L)

- 8.1.5 Calculate the cyanide of solid samples in mg/kg of original sample, as follows:
- 8.1.5.1 A separate determination of percent solids must be performed (See Part F).

8.1.5.2 The concentration of cyanide in the sample is determined using Equation 2:

EQ. 2,

$$CN, (mg/Kg) = \frac{A \times D \times F}{B \times E}$$

where,

A = ug/L CN of sample from regression analysis curve
B = wet weight of original sample in g (See Section 7.1.3)
D = Dilution factor (If no dilution is performed, D = 1)
E = % solids (See Part F)/100.
F = sample receiving solution volume (0.050 L)

9.0 Quality Control

Quality control shall be performed as specified in Exhibit E.

PART F - PERCENT SOLIDS DETERMINATION PROCEDURE

- 1.0 Prior to initiating sample preparation for analysis, determine the sample's percent moisture. Weigh 5 - 10 g of the soil/sediment/solid into a pre-weighed weighing dish. Weigh and record the weight to the nearest 0.01 g.
- 2.0 Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven maintained at 103-105°C. Sample handling and drying should be conducted in a well-ventilated area.
- 3.0 Dry the sample overnight (12-24 hours) but no longer than 24 hours. If dried less than 12 hours, it must be documented that constant weight was attained.* Remove the sample from the oven and cool in a dessicator with the weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 g. Do not analyze the dried sample.
- 4.0 Duplicate percent solids determinations are required at the frequency specified in Exhibit E for duplicate determination. Duplicate results must meet the technical acceptance specified in Exhibit E and shall be recorded on FORM VI as indicated in Exhibit B.
- 5.0 For the duplicate percent solids determination, designate one sample aliquot as the "original" sample and the other aliquot as the "duplicate" sample. Calculate dry weight using the results of the "original" sample aliquot.
- 6.0 Calculate percent solids by the formula below. The value obtained shall be reported on the appropriate FORM I and, where applicable, FORM VI. This value will be used for calculating analytical concentration on a dry weight basis.

EQ. 1

$$\% \text{ Solids} = \frac{\text{Sample Dry Weight (g)}}{\text{Sample Wet Weight (g)}} \times 100$$

- 6.1 If the percent solids of the sample as determined above is greater than 30 percent (> 30%), the Contractor shall proceed with preparation and analysis for soil/sediment/solid samples as described Exhibit D.

*For the purpose of paragraph 3, drying time is defined as the elapsed time in the oven; thus raw data must record time in and out of the oven to document the 12 hour drying time minimum. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/dessicate/weigh cycles with a minimum of 1 hour drying time in each cycle. Constant weight would be defined as a loss in weight of no greater than 0.01 g between the start weight and final weight of the last cycle.

- 6.2 If the percent solids of the soil/sediment/solid sample is less than or equal to 30 percent ($\leq 30\%$), then centrifuge and decant or filter the sample to remove the majority of the water. Determine the percent solids of the remaining centrifuged/filtered solid sample. If the percent solids of the centrifuged or filtered soil/sediment/solid sample is greater than 30 percent ($> 30\%$), proceed with preparation and analysis of the centrifuged/filtered sample using the soil/sediment/solid sample method as described in Exhibit D.
- 6.2.1 If the percent solids of the centrifuged/filtered soil/sediment/solid sample is less than or equal to 30 percent ($\leq 30\%$), then the Contractor shall contact the RSCC for directions. The Region may require that the Contractor do one of the following:
- Analyze the centrifuged/filtered soil/sediment/solid sample "as is";
 - Use an additional aliquot (weight) of centrifuged soil/sediment/solid sample ($\leq 30\%$ S) for preparation and/or decrease the final digestate volume to achieve the dry weight CRQLs;
 - Use another method of analysis;
 - Do not analyze that sample.
- 6.2.2 If the percent solids of the centrifuged/filtered soil/sediment/ solid sample is less than 10 percent ($< 10\%$), then the Contractor must contact the RSCC for directions. The Region may require that the Contractor do one of the following:
- Analyze the soil/sediment/solid sample ($< 10\%$ S) "as is";
 - Use an additional aliquot (weight) of soil/sediment/solid sample ($< 10\%$ S) for preparation and/or decrease the final digestate volume to achieve the dry weight CRQLs;
 - Use another method of analysis;
 - Do not analyze that sample.
- 6.2.3 If a sufficient sample amount has not been provided by the sampler to perform the additional percent solids determinations and/or to analyze an increased portion of sample, then the Contractor shall contact the RSCC to ascertain whether or not the sample should be analyzed.
- 6.3 For all samples that do not meet the greater than 30 percent solids ($> 30\%$ S) requirement, the Contractor shall note the problem, the EPA sample numbers for the affected samples, the initial and subsequent percent solid(s), the steps taken to achieve the dry weight CRQLs including the weight/volume/percent solids of the sample prepared and analyzed, the final digestate volume, and the Region's instructions in the SDG Narrative.

Exhibit D -- Section IV

Part F - Percent Solids Determination

PART G - DETERMINATION OF TOTAL ORGANIC CARBON

Table of Contents

<u>Method</u>	<u>Page No.</u>
Determination of Total Organic Carbon in Water and Wastewater	D-94
Determination of Total Organic Carbon in Soil and Sediment	D-108

DETERMINATION OF TOTAL ORGANIC CARBON IN WATER AND WASTEWATER

1.0 SCOPE AND APPLICATION

The analytical method that follows is designed to measure the amount of organic carbon in water and wastewater. The persulfate-ultraviolet oxidation method employed here, is a rapid and precise technique for the measurement of trace levels of organic carbon. A minimum concentration of 50 µg organic carbon/L can be quantitatively measured. This method is, however, limited to applications where the carbonaceous matter is either soluble or has a particle size of 0.2 mm or less. The method is based on *EPA Methods for Chemical Analysis of Water and Wastes*, Method 415.2, Revised 1983, and *Standard Methods for the Examination of Water and Wastewater*, 18th Edition, 1992, Method 5310 C, and has been modified for EPA New England.

2.0 SUMMARY OF METHOD

Two comparable detection systems for the determination of organic carbon in aqueous samples are described below.

2.1 Flame ionization gas chromatography detection, after catalytic conversion of organic carbon to methane

A portion of aqueous sample is combined with an acidified persulfate reagent and placed in a sparging vessel. The sample is purged with helium which transfers inorganic CO₂ and purgeable organics to a CO₂ scrubber. (The acid in the persulfate reagent converts carbonates and bicarbonates to CO₂ which are removed by the scrubber with at least 99.9% efficiency over a 2.5 minute purge.) The purgeable organics proceed through the scrubber and into a reduction system where the gas stream is joined by hydrogen and passed over a nickel catalyst which converts the purgeable organic carbon to methane. The methane is then measured by a flame ionization detector.

The purged sample is then transferred to a quartz ultraviolet reaction coil where the nonpurgeable organics are subjected to intense ultraviolet illumination in the presence of the acidified persulfate reagent. The nonpurgeable organics are converted to CO₂. The sample is then transferred to a second sparger where a helium purge transfers the CO₂ to the reduction system (where the CO₂ is converted to methane) and then into the detector where the methane is measured.

2.2 Direct non-dispersive infrared detection

An aliquot of acidified sample is placed in the sparging vessel. The sample is purged with helium which transfers inorganic CO₂ and purgeable organics to a CO₂ scrubber. (The acid converts carbonates and bicarbonates to CO₂ which are removed by the scrubber with at least 99.9% efficiency over a 2.5 minute purge.) The purge gas, containing the purgeable organics, proceeds through the scrubber and into a quartz ultraviolet reactor that is filled with a constant-feed persulfate solution. In the presence of persulfate, the intense ultraviolet illumination oxidizes the organic carbon to CO₂. The CO₂ produced is sparged continuously from the solution and is carried in the gas stream to an infrared analyzer that is specifically tuned to the absorptive wavelength of CO₂.

The portion sparged sample is then transferred directly into the ultraviolet reactor where the nonpurgeable organics are oxidized to CO₂ and sparged into the infrared analyzer.

Exhibit D -- Section IV
Part G - Total Organic Carbon in Water and Wastewater

2.3 Method Detection Limits (MDLs)

Prior to sample analysis, method detection limits (MDLs) must be determined for each instrument used for determining total organic carbon in accordance with Exhibit E. The MDL value must meet the CRQL requirements in Exhibit C.

3.0 DEFINITIONS

3.1 Total organic carbon measured by this procedure is the sum of the purgeable organic carbon and the nonpurgeable organic carbon as defined in 3.2 and 3.3.

3.2 Purgeable organic carbon is the organic carbon matter that is transferred to the gas phase when the sample is purged with helium and which passes through the CO₂ scrubber.

3.3 Nonpurgeable organic carbon is defined as that which remains after removal of the inorganic carbon and the purgeable organic carbon.

4.0 SAMPLE HANDLING AND PRESERVATION

Samples must be collected in 4 oz. glass jars with Teflon lined caps. The samples must be acidified with sulfuric acid to pH 2 at the time of collection and must be taken without headspace to prevent the loss of purgeable organics. Cool and maintain samples at 4°C until the time of analysis. Samples must be analyzed within 26 days from the verified time of sample receipt (VTSR).

5.0 INTERFERENCES

5.1 If a sample requires homogenization in a blender to reduce the size of the particulate matter, the homogenizing may cause loss of purgeable organic carbon, thus yielding erroneously low results

5.2 The intensity of the ultraviolet light reaching the sample matrix may be reduced by highly turbid samples or with aging of the ultraviolet source, resulting in sluggish or incomplete oxidation.

5.3 Persulfate oxidation of organic molecules is slowed in samples containing significant concentrations of chloride by the preferential oxidation of chloride; at a concentration of 0.1% chloride, oxidation of organic matter may be inhibited completely. To remove this interference add mercuric nitrate to the persulfate solution.

5.4 With any organic carbon measurement, contamination during sample handling and treatment is a likely source of interference.

6.0 APPARATUS

6.1 Balance - analytical, capable of accurately weighing ± 0.0001 g. The balance must be calibrated in accordance with ASTM E 617 specifications each 8-hour work shift. The balance must also be checked annually by a certified technician. All balance checks and maintenance must be recorded in a bound logbook and a copy of this information must be submitted with the sample data package.

6.2 Apparatus for blending or homogenizing samples: A household blender or similar device that will reduce particles in the sample to less than 0.2 mm.

6.3 Analytical instrument options:

No specific analyzer is recommended as superior. The instruments listed in Sections 6.3.1 and 6.3.2 are for informational purposes only and are not intended to restrict the use of other instruments capable of analyzing TOC.

6.3.1 Dohrmann Envirotech DC-54 Carbon Analyzer, or equivalent.

The essential components for the apparatus used in this method are: A sparge assembly, flow switching valves, a pyrolysis furnace, quartz ultraviolet reactor coil, reducing column, flame ionization detector, electrometer and integrator.

6.3.2 Dohrmann DC-80 Carbon Analyzer, or equivalent.

The essential components for the apparatus used in this method are: A sparge assembly, quartz ultraviolet reactor, non-dispersive infrared analyzer, electrometer and integrator.

6.4 Assorted Pipets

6.5 Syringes - 50 μ L, 250 μ L, and 1000 μ L capacity

7.0 REAGENTS

7.1 Distilled or deionized water - ultra pure for preparation of standards and for dilution of samples.

7.2 Acidified Persulfate Reagent. To 100 mL of distilled or deionized water, add 5 g of potassium persulfate and 3 mL of concentrated (85%) phosphoric acid.

Note: The acidified persulfate reagent is for use with the procedure incorporating the TOC analyzer described in Section 6.3.1. For the persulfate reagent required for the TOC analyzer described in Section 6.3.2, refer to the manufacturer's instructions for reagent preparation.

7.3 Stock Standards

7.3.1 Potassium hydrogen phthalate, stock solution, (1000 mg carbon/L). Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled or deionized water and dilute to 100 mL in a volumetric flask.

7.3.2 Carbonate-bicarbonate, stock solution (1000 mg carbon/L). Dissolve 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate in distilled or deionized water and dilute to 100 mL in a volumetric flask.

7.4 Secondary dilution standard

Prepare a secondary dilution standard by diluting the potassium hydrogen phthalate stock solution (7.3.1) with distilled or deionized water. The secondary dilution standard should be prepared at a concentration that can be easily aliquoted to prepare the initial and continuing calibration standards.

Exhibit D -- Section IV
Part G - Total Organic Carbon in Water and Wastewater

7.5 Working Standards

All working standards must be prepared fresh daily prior to analysis.

7.5.1 Initial Calibration Standards

Prepare a series of five initial calibration standards, including a blank and four standards, by pipetting appropriate volumes of the secondary standard solution (7.4) into separate 100 mL volumetric flasks and diluting to volume. The low standard (not including the blank) must be prepared at a concentration equal to the CRQL (50 µg/L). The high calibration standard shall define the linear range for the analysis and the remaining standards shall be at graduated intervals between the low and high standards.

7.5.2 Continuing Calibration standard

Prepare a continuing calibration standard from the secondary dilution standard at a concentration equal to a mid-point standard in the calibration curve.

7.5.3 Initial Calibration Verification Standard

Prepare an initial calibration verification standard at a concentration near the mid-range of the calibration curve, but not equal to the any of the initial calibration standards. The initial calibration verification standard must be prepared from a source other than that used to prepare the initial calibration standards (e.g. second source verification).

7.5.4 Carbonate-bicarbonate, standard solution (50 mg carbon/L). Pipet 5 mL of the carbonate-bicarbonate stock solution in a 100 mL volumetric flask and dilute to volume with distilled or deionized water.

7.5.5 Laboratory Fortified Blank

Prepare a Laboratory Fortified Blank (LFB) containing potassium hydrogen phthalate at a concentration equal to the CRQL. One LFB must be prepared and analyzed with each batch of samples prepared and analyzed.

8.0 PROCEDURE

8.1 Sample Preparation

8.1.1 If insufficient sample volume (less than 90% of the required volume) is received to perform the analyses, the Contractor shall contact the RSCC for instructions. The Region will either require that sample analyses not be performed or will require that a reduced volume be used for the sample analysis. Changes in the sample analysis must be preapproved by the Region. The Contractor shall document the problem, EPA sample numbers for the affected samples, and the Region's instructions (including sample volume prepared and analyzed) in the SDG Narrative.

8.1.2 If multiphase samples (e.g., two-phase liquid sample) are received by the Contractor, then the Contractor shall notify the RSCC that a multiphase sample has been received.

8.1.2.1 If all phases of the sample are amenable to analysis, the Region may require the Contractor to do one of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze each phase separately. The RSCC will provide EPA sample numbers for the additional phases, if required.
- Separate the phases of the sample and analyze one or more of the phases, but not all of the phases. The RSCC will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

8.1.2.2 If all of the phases are not amenable to analysis (i.e., outside scope of the method), then the Region may require the Contractor to do one of the following:

Exhibit D -- Section IV

Part G - Total Organic Carbon in Water and Wastewater

- Separate the phases and analyze the phase(s) that is amenable to analysis. The RSCC will provide EPA sample numbers for the additional phases, if required.
 - Do not analyze the sample.
- 8.1.2.3 The Contractor shall document the problem, the EPA sample numbers for the affected samples, and the Region's instructions in the SDG Narrative.
- 8.1.3 If the sample contains gross particulate or insoluble matter, homogenize the sample in a blender for approximately 1 minute until a representation portion can be aliquoted through a pipet and/or syringe needle.
- 8.1.4 All aqueous samples must be allowed to warm to ambient temperature before aliquoting for analysis. If any sample containers contain air bubbles, the Contractor shall document the problem, the size of the air bubble, and the EPA sample numbers for the affected samples in the SDG Narrative. If multiple containers are provided for that sample, then the Contractor shall use the sample container which does not contain air bubbles.
- 8.1.5 pH Determination
- Prior to taking the sample aliquots, the pH of the aqueous sample must be checked. The purpose of the pH determination is to ensure that all TOC samples were acidified in the field. Test the pH by placing one or two drops of sample on the pH paper (do **not** add pH paper to the sample container). If the sample pH is greater 2, adjust to pH 2 by the addition of 1:1 sulfuric acid or 1:1 phosphoric acid. Note the samples which required pH adjustment in the SDG Narrative.
- 8.1.7 Aqueous sample analysis
- Prior to aliquoting samples for preparation and analysis, establish the appropriate TOC operating conditions and calibrate the analyzer as outlined in Section 7.2. This should be done to avoid loss of purgeable organics.
- For the carbon analyzer described in Section 6.3.1, add 1 mL of acidified persulfate reagent (7.6) to 50 mL of sample. For the carbon analyzer described in Section 6.3.2 no acidified persulfate reagent is required.
- 8.1.7.1 Aliquot 10 ml of sample into a sparging vessel and proceed with the purgeable organics analysis following the manufacturer's instructions.
- 8.1.7.2 Following the purgeable organics determination, analyze the purged sample (or an aliquot of the purged sample) for nonpurgeable organics in accordance with the manufacturer's instructions.
- 8.2 Calibration and Analysis
- 8.2.1 Allow at least 30 minutes instrument warm-up time. Follow the manufacturer's instructions for assembly/set-up, testing, calibration, and operation.
- 8.2.2 Prepare the series of initial calibration standards specified in Section 7.5.1. If the carbon analyzer described in Section 6.3.1 is being used, add 1 mL of acidified persulfate reagent (7.2) to 50 mL of calibration standard.
- 8.2.3 Calibrate the instrument using the blank and the four calibration standards that define the analytical range. Prepare a calibration curve plotting μg carbon vs. instrument response. The calibration curve must meet the criteria for linearity specified in Exhibit E, to continue the analysis.
- 8.2.3.1 NOTE: The blank and standards that make up the calibration curve, may be analyzed directly, omitting the purgeable organics determination, if
- The response of the blank (analyzed directly) is less than or equal to one half the response of the lowest standard (50 μg carbon/L, analyzed directly), or

Exhibit D -- Section IV
Part G - Total Organic Carbon in Water and Wastewater

- The response of the blank (analyzed directly), after acidifying and purging the standard, is the same as analyzing the blank directly without purging.

Otherwise, all calibration blanks and standards must be analyzed for both purgeable and nonpurgeable organics.

8.2.3.2 If the TOC analyzer prevents the required 5 point calibration, calibrate according to the instrument manufacturer's recommendations, and analyze the remaining required standards immediately after calibration. The results of all additional standards (except the low standard at the CRQL) shall be within $\pm 20\%$ of the true value. The CRQL standard must be within \pm CRQL value. The concentration of each standard and the calculations to show that the recovery criteria have been met shall be documented in the raw data.

8.2.3.3 If the values do not fall within this range, the instrument must be recalibrated and the additional standards reanalyzed. The additional standards must meet the criteria specified in Section 8.2.3.2 before any samples, QC samples and required blanks are analyzed.

8.2.4 After the instrument has been calibrated, the analytical sequence that is outlined below and described in Exhibit E must be followed. In addition, the quality control criteria specified in Section 10.0 must be adhered to. The results of these analyses must meet the acceptance criteria specified in Exhibit E and Section 10.0 to continue the analysis.

Note, if the criteria in Section 8.2.3.1 were met, the ICV and CCV calibration verification standards may be analyzed directly, omitting the purging step. The ICB and CCB, however, must be analyzed for both purgeable and nonpurgeable organics to determine if contamination is present in either step of the analysis process.

8.2.4.1 Analytical Sequence Summary

- Initial Calibration (blank and 4 standards)
- ICV, ICB, LFB, carbonate-bicarbonate check standard (see Section 10.2), CCV, CCB
- 10 analytical samples, maximum (all samples must be analyzed in duplicate)
- CCV, CCB (repeated every 10 analytical samples, but not greater than every 2 hours)
- Last analytical sample, carbonate-bicarbonate check standard, LFB, CCV, CCB.

8.3 Sample Dilutions

8.3.1 Use the results of the original analysis to determine the approximate dilution factor required to bring the response within the initial calibration range.

8.3.2 The dilution factor chosen should keep the response in the upper half of the initial calibration range of the instrument.

8.3.3 All dilutions of aqueous samples are prepared in volumetric flasks (10 mL to 100 mL).

8.3.4 Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

8.3.5 Calculate the approximate volume of distilled or deionized water which will be added to the volumetric flask selected and add slightly less than this quantity to the flask.

8.3.6 Pipet the proper aliquot of sample into the volumetric flask and dilute to the mark with distill or deionized water. Cap the flask and invert three times.

Exhibit D -- Section IV

Part G - Total Organic Carbon in Water and Wastewater

8.3.7 If this is an intermediate dilution, use it and repeat the above procedure to further dilute the sample.

8.3.8 Analyzed the diluted sample in accordance with Section 8.0.

9.0 CALCULATIONS

Determine the concentration of Total Organic Carbon, $\mu\text{g/L}$, for each sample, QC sample, and required blank using Equation 1.

Exhibit D -- Section IV
Part G - Total Organic Carbon in Water and Wastewater

EQ. 1

$$\text{Total Organic Carbon } (\mu\text{g/L}) = \frac{(\text{POC}) (Df_1)}{V_1} + \frac{(\text{NPOC}) (Df_2)}{V_2}$$

Where,

POC = Purgeable Organic Carbon determined from calibration curve, μg
NPOC = Nonpurgeable Organic Carbon determined from calibration curve, μg
 V_1 = Volume of sample purged for POC determination, L
 V_2 = Volume of sample purged or injected for NPOC determination, L
 Df_1 = Dilution factor for purgeable fraction (If no dilution is performed, $Df_1 = 1$)
 Df_2 = Dilution factor for nonpurgeable fraction (If no dilution is performed, $Df_2 = 1$)

10.0 QUALITY CONTROL

10.1 Blanks

There are three types of blanks required by this method: the initial calibration blank (ICB), continuing calibration blank (CCB), and preparation blank.

The ICB and CCB consist of a volume of distilled or deionized water that is acidified to pH of 2 and analyzed in the same manner as the analytical standards. The results of the ICB and CCB analyses indicate whether there is contamination in the system from a previous sample.

The preparation blank consists of a volume of distilled or deionized water that is acidified to pH of 2. The preparation blank is prepared and analyzed in the identical manner as the samples in the SDG. If additional preparation techniques are used, such as blender homogenization, the preparation blank must be subjected to the same techniques. The purpose of a preparation blank is to determine the levels of contamination associated with the processing and analysis of samples.

10.1.1 Frequency

All blanks (ICB, CCB, preparation blank) must be analyzed at the frequency specified in Exhibit E and must be analyzed for both purgeable and nonpurgeable organic carbon.

10.1.2 Procedure

Prepare and analyze all blanks in accordance with Section 8.0 and Exhibits E.

10.1.3 Calculations

Determine the total organic carbon content for each blank using Equation 1.

10.1.4 Technical Acceptance Criteria

All blanks must be prepared and analyzed at the frequency described in Section 10.1.1 and must meet the acceptance criteria specified in Exhibit E for blank analyses.

10.1.5 Corrective Action

If the technical acceptance criteria for blank analyses are not met, then the contractor must stop and correct the problem before continuing.

Any blank that fails to meet the technical acceptance criteria as specified in Section 10.1.1 and Exhibit E for blank analyses must be reanalyzed at no additional cost to the Agency. Furthermore, all samples, including the duplicate and matrix spike samples, associated with the blank that does not meet the technical acceptance criteria for blanks must also be reanalyzed at no additional cost to the Agency.

If sample analyses are reported with non-compliant blanks, then the contractor shall receive a commensurate reduction in sample price depending upon the impact of the non-compliance on data usability.

10.2 Carbonate-Bicarbonate Check Standard

The carbonate-bicarbonate check standard analysis provides information regarding the efficiency of the CO₂ scrubber used in-line with the purgeable organic carbon determination. The in-line scrubber is present to remove inorganic carbon (carbonate and bicarbonate that is converted to CO₂ during sample acidification) from the sample being purged.

10.2.1 Frequency

The carbonate-bicarbonate check standard analysis shall be required for the purgeable organic carbon determination. The check standard must be analyzed prior to the analysis of any samples, QC samples or required blanks, and after the last sample in the analytical sequence (refer to the analytical sequence summary, Section 8.2.4.1). The analysis conditions for the carbonate-bicarbonate check standard must be the same as those for the analytical samples.

10.2.2 Procedure

Follow the procedures specified in Section 8.0 for the preparation and analysis of the carbonate-bicarbonate check standard. Results of carbonate-bicarbonate check standard analyses shall be reported on FORM 2A.

10.2.3 Calculations

Determine the concentration of any inorganic carbon that passed through the scrubber in mg/L using Equation 2.

EQ. 2

$$\text{Inorganic Carbon } (\mu\text{g/L}) = \frac{IC}{V}$$

Where,

IC = Inorganic carbon passing the CO₂ scrubber, μg
V = Volume of sample purged, L

Exhibit D -- Section IV
Part G - Total Organic Carbon in Water and Wastewater

10.2.4 Technical Acceptance Criteria

Carbonate-bicarbonate check standards must be prepared and analyzed at the frequency described in Section 10.2.1.

- 10.2.4.1 The concentration of inorganic carbon passing the CO₂ scrubber must be less than the CRQL.

10.2.5 Corrective Action

If the carbonate-bicarbonate check standard analysis does not meet the technical acceptance criteria in Section 10.2.4, the analysis shall be stopped, the problem determined and the carbonate-bicarbonate check standard must be reanalyzed. The carbonate-bicarbonate check standard analysis must meet the technical acceptance prior to the analysis of any samples, QC samples or required blanks for purgeable organic carbon. Furthermore, all samples, QC samples or required blanks analyzed up until the last compliant carbonate-bicarbonate check standard must also be reanalyzed at no additional cost to the Agency.

If sample analyses are reported with non-compliant carbonate-bicarbonate check standards, then the contractor shall receive a commensurate reduction in sample price depending upon the impact of the non-compliance on data usability.

10.3 Duplicate Sample Analysis (D)

The duplicate sample analysis provides information regarding the precision of the preparation and analysis procedures. Duplicate analyses shall be reported on FORM 1B.

10.3.1 Frequency

Each sample in the Sample Delivery Group (SDG) shall be analyzed in duplicate. Duplicate analyses are required for both the purgeable and nonpurgeable fractions of the TOC analysis.

10.3.2 Procedure

Follow the procedures as specified in Section 8.0 for the preparation and analysis of the original and duplicate samples.

10.3.4 Calculations

- 10.3.4.1 Determine the total organic carbon content in the original and duplicate samples using Equation 1.

- 10.3.4.2 Calculate the Relative Percent Difference (RPD) between the original and duplicate sample using Equation 3 below. Report RPD results on Form 1B as described in Exhibit E.

EQ. 3

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where,

RPD = Relative Percent Difference
S = Sample result (original), µg/L
D = Duplicate sample result, µg/L

10.3.5 Technical Acceptance Criteria

Duplicate samples must be prepared and analyzed at the frequency described in Section 10.3.1 and must meet the acceptance criteria specified in Exhibit E for duplicate analyses.

10.3.6 Corrective Action

Samples that do not meet the technical acceptance criteria for duplicate analysis shall be reanalyzed, once, at no additional cost to the Agency.

An original and duplicate of that sample must be reanalyzed. Report both the original and duplicate results for both the original analysis and the re-analysis on Form 1B as described in Exhibit B. If an RPD result does not meet the acceptance criteria, flag the result with an "*" on FORM 1B.

- 10.3.6.1 Duplicate samples **must** be prepared and analyzed for every sample in an SDG. If duplicates are not prepared and analyzed for every sample in an SDG, the contractor shall reprepare and reanalyzed those samples not analyzed in duplicate at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample acceptance criteria.
- 10.3.6.2 Sample results reported without duplicate analyses shall be receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data usability.

10.4 Spike Sample Analysis (S)

10.4.1 Summary

In order to evaluate the effects of the sample matrix and to determine the precision of the method used for TOC determination, a sample must be spiked with organic carbon and analyzed in accordance with the method.

10.4.2 Frequency of Spike Analysis

- 10.4.2.1 A spiked sample analysis must be performed for each group of samples of a similar matrix for the following, whichever is most frequent:
 - Each SDG (not to exceed 20 field samples), or
 - Each matrix within an SDG, or
 - EPA may require additional MS analyses, upon Regional request, for which the Contractor will be paid.
- 10.4.2.2 As a part of the Agency's QA/QC program, aqueous equipment and/or field blanks may accompany water samples that are delivered to a laboratory for analysis. The Contractor shall not perform the spike analysis on any of the designated field QC samples.
- 10.4.2.3 The Contractor shall not perform the spike analysis on any designated Performance Evaluation samples.
- 10.4.2.4 If the EPA Region designates a sample to be used as a spiked sample, then that sample must be used. If there is insufficient sample volume to perform a spike analysis, then the Contractor shall contact the RSCC to ascertain an alternate sample to be used for the spike analysis. The EPA sample numbers, the Region's instructions, and date of contact must be included in the SDG Narrative.
- 10.4.2.5 If there is insufficient sample volume in any of the samples in an SDG to perform a spike analysis, then the Contractor shall immediately contact the RSCC to report the problem. The Region will either approve that no spiked sample is required, or require that a reduced sample aliquot be used for the unspiked sample and the spiked sample analysis, or that the unspiked sample is analyzed at full volume and the spiked sample is analyzed at reduced volume. The RSCC will notify the Contractor of the resolution. The Contractor shall document the decision in the SDG Narrative.
- 10.4.2.6 If the Contractor has a question regarding the frequency, etc., of the spike analysis for a particular SDG, contact the RSCC for clarification.

10.4.3 Procedure for Preparing a spiked sample

To prepare a spike sample, add 25 µL of the potassium hydrogen phthalate stock solution (Section 7.3.1) to 50 mL of the sample chosen for spiking. Process the sample according to Section 8. Disregarding any dilutions, this is equivalent to a concentration of 500 µg/L of the spiked compound.

- 10.4.3.1 Before performing a spike analysis, analyze the sample used for spiking. If the sample analysis required a dilution to bring the sample results

Exhibit D -- Section IV
Part G - Total Organic Carbon in Water and Wastewater

within the calibration range, then the spiked sample should be prepared using the same dilution for which the sample results will be reported to the Agency.

10.4.4 Calculations for Spiked Sample Analysis

10.4.4.1 Calculate the TOC concentration of the spiked sample using Equation 1.

10.4.4.2 Calculate the recovery of the spiked compound using equation 4.

EQ. 4

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spiked sample result
SR = Sample result
SA = Spike added

10.4.5 Technical Acceptance Criteria for Spike Sample Analysis

10.4.5.1 All Spiked samples must be analyzed on a TOC system meeting the initial calibration, initial calibration verification, and continuing calibration technical acceptance criteria defined in Exhibit E.

10.4.5.2 The Spiked samples must be analyzed or reanalyzed within the contract required holding time defined in Section 4.

10.4.5.3 All spiked samples must have an associated preparation blank, and ICB and CCB blanks that meet the blank technical acceptance criteria defined in Exhibit E.

10.4.5.4 The technical acceptance criteria for spiked sample recoveries are given in Exhibit E. These limits are advisory and no further action by the laboratory is required. However, frequent failures to meet the limits for recovery warrant investigation by the laboratory, and may result in questions from the Agency.

10.4.6 Corrective Action for Spiked Sample Analysis

Any spiked sample that does not meet the technical acceptance criteria for spiked sample analysis must be reanalyzed at no additional cost to the Agency. Both sets of data must be reported on separate Forms 5A and must distinguish between the initial analysis and the reanalysis using the suffixes in Exhibit B.

10.4.6.1 Corrective actions for failure to meet initial and continuing calibration and initial calibration verification must be completed before the analysis of any QC samples.

10.4.6.2 Corrective actions for failure to meet all blank technical acceptance criteria must be met before the analysis of any QC samples.

10.4.6.3 The contractor must make every effort to reanalyze the sample within the contract required holding times.

10.5 Laboratory Fortified Blank (LFB)

The Laboratory Fortified Blank (LFB) analysis verifies the accuracy at the Contract Required Quantitation Limit. The concentration of the LFB shall be at the CRQL.

10.5.1 Frequency

One LFB must be prepared and analyzed with each batch of samples prepared and analyzed. The LFB must be analyzed after the initial calibration blank, prior to the analysis of any samples, and after the last sample in the analytical sequence (refer to the analytical sequence summary, Section

Exhibit D -- Section IV

Part G - Total Organic Carbon in Water and Wastewater

8.2.4.1). The preparation and analysis conditions for the LFB must be the same as those for the analytical samples.

10.5.2 Procedure

Prepare an LFB at a concentration equal to the CRQL using potassium hydrogen phthalate standard (section 7.3.1). Process the LFB according to procedures specified in Section 8.0.

10.5.3 Calculations

Calculate the percent recovery of the LFB using Equation 5:

Exhibit D -- Section IV
Part G - Total Organic Carbon in Water and Wastewater

EQ. 5

$$\text{Percent Recovery (\%R)} = \frac{M}{T} \times 100$$

Where,

M = Measured analyte concentration

T = True analyte concentration.

10.5.4 Technical Acceptance Criteria

The LFB must be prepared and analyzed at the frequency described in Section 10.5.1. The LFB must meet the acceptance criteria specified in Exhibit E for LFB analyses.

10.5.5 Corrective Action

If the LFB does not meet the technical acceptance criteria in Section 10.5.4, then the analysis shall be terminated, the problem corrected and the samples associated with that LFB redigested and reanalyzed. The LFB analysis must meet the technical acceptance prior to the analysis of any samples, QC samples or required blanks. Furthermore, all samples, QC samples or required blanks analyzed up until the last compliant LFB must also be reanalyzed at no additional cost to the Agency.

If sample analyses are reported with non-compliant LFB analyses, then the contractor shall receive a commensurate reduction in sample price depending upon the impact of the non-compliance on data usability.

DETERMINATION OF TOTAL ORGANIC CARBON IN SOIL AND SEDIMENT

1.0 SCOPE AND APPLICATION

The analytical method that follows is designed to measure the amount of organic carbon in soil and sediments. Although the detection limit may vary with procedure or instrument, a minimum dry weight reporting value of 100 mg/kg shall be required. Wet combustion methods are not considered to be equivalent to the pyrolytic methods herein described. This method is based on the *Lloyd Kahn Method for Determination of Total Organic Carbon in Sediment*. U.S. EPA, Region II. July 1986. The method has been modified for EPA New England.

2.0 SUMMARY OF METHOD

- 2.1 A portion of well mixed sample (up to 500 mg) is first treated with an acid solution to remove inorganic carbon. (The acid converts carbonates and bicarbonates in the sample to CO₂ which driven off by heating the sample to 75°C for 1 hour.) The organic compounds in the sample are then decomposed by pyrolysis in the presence of oxygen or air. The carbon dioxide that is formed is determined by:

- Direct non-dispersive infrared detection,
- Flame ionization gas chromatography after catalytic conversion of the carbon dioxide to methane,
- Thermal conductivity gas chromatography,
- Differential thermal conductivity detection by sequential removal of water and carbon dioxide, or
- Thermal conductivity detection following removal of water with magnesium perchlorate.

- 2.2 Water content is determined on a separate portion of soil/sediment.

2.3 Method Detection Limits (MDLs)

Prior to sample analysis, method detection limits (MDLs) must be determined for each instrument used for determining total organic carbon in accordance with Exhibit E. The MDL value must be determined in total mg carbon and state the minimum dry weight of sample that must be analyzed to obtain the CRQL requirement in Exhibit C.

3.0 SAMPLE HANDLING AND PRESERVATION

Collect soil/sediments in 4 oz. glass jars with Teflon or aluminum foil lined caps. Cool and maintain samples at 4°C until the time of analysis. Samples must be analyzed within 12 days from the verified time of sample receipt (VTSR).

4.0 INTERFERENCES

- 4.1 Volatile organics in the soil/sediments may be lost in the decarbonation step resulting in a low bias.
- 4.2 Bacterial decomposition and volatilization of the organic compounds are minimized by maintaining the sample at 4°C, analyzing the sample within the specified holding time, and analyzing the sample as received.

5.0 APPARATUS

5.1 Balance - top loading, capable of weighing accurately to ± 0.01 g, analytical, capable of accurately weighing ± 0.0001 g. The balance must be calibrated in accordance with ASTM E 617 specifications each 8-hour work shift. The balance must also be checked annually by a certified technician. All balance checks and maintenance must be recorded in a bound logbook and a copy of this information must be submitted with the sample data package.

5.2 Oven - capable of being regulated to a constant temperature of $105 \pm 5^\circ\text{C}$. The 105°C oven temperature must be checked daily, prior to use, using a second source thermometer. The second source thermometer temperature must agree within $\pm 2^\circ\text{C}$ of the oven thermometer or digital readout. If this limit is not met, then the problem thermometer must be determined and replaced, or if the oven uses a digital readout, the digital readout must be recalibrated or a compliant thermometer must be used in its place. All thermometers must be checked at least annually against a primary reference thermometer. All thermometer checks must be recorded in a bound logbook and a copy of this information must be submitted with the sample data package.

5.3 Analytical instrument options:

No specific analyzer is recommended as superior. The instruments listed in Sections 5.3.1 through 5.3.4 are for informational purposes only and are not intended to restrict the use of other unlisted instruments capable of analyzing TOC. Instruments used must have the following minimum specifications:

- A combustion boat which is heated in a stream of oxygen or air in a resistance or induction-type furnace to completely convert organic substances to CO_2 and water.
- A means to, physically or by measurement technique, separate water and other interferants from CO_2 .
- A means to quantitatively determine CO_2 with adequate sensitivity (100 mg/kg, dry weight basis), and precision (25% at the 95% confidence level as demonstrated by repetitive measurements of a well mixed soil/sediment sample).

5.3.1 Perkin Elmer Model 240C Elemental Analyzer or equivalent.

In this instrument, the sample is pyrolyzed under pure oxygen, water is removed by magnesium perchlorate and the carbon dioxide is removed by ascarite. The decrease in signal obtained by differential thermal conductivity detectors placed between the combustion gas stream before and after the ascarite tube is a measure of the organic carbon content.

5.3.2 Carlo Erba Model 1106 CHN Analyzer, or equivalent.

In this instrument, the sample is pyrolyzed in an induction type furnace, and the resultant carbon dioxide is chromatographically separated and analyzed by a differential thermal conductivity detector.

5.3.3 LECO Models WR12, WR112, or CR-12 carbon determinators, or Models 600 or 800 CHN analyzers, or equivalent.

Exhibit D -- Section IV

Part G - Total Organic Carbon in Soil and Sediment

- 5.3.3.1 In the LECO WR-12, the sample is burned in a high frequency induction furnace and the carbon dioxide is selectively absorbed at room temperature in a molecular sieve. It is subsequently released by heating and is measured by a thermal conductivity detector. The WR-112 is an upgraded WR-12 employing microprocessor electronics and a printer to replace the electronic digital voltmeter.
 - 5.3.3.2 In the LECO CR-12 carbon determinator, the sample is combusted in oxygen, moisture and dust are removed by appropriate traps and the carbon dioxide is measured by a selective, solid state, infrared detector. The signal from the detector is then processed by a microprocessor and the carbon content is displayed on a digital readout and recorded on an integral printer.
 - 5.3.3.3 In the LECO CHN-600 and CHN-800 elemental analyzers, the sample is burned under oxygen in a resistance furnace and the carbon dioxide is measured by a selective infrared detector.
 - 5.3.4 Dohrmann Model DC85 Digital High Temperature TOC Analyzer, or equivalent.
In this instrument, the sample is burned in resistance furnace under oxygen, the interfering gases are removed by a sparger/scrubber system and the carbon dioxide is measured by a non-dispersive infrared detector and shown on a digital display in concentration units.
 - 5.4 A strip chart or other permanent recording device to document the analysis.
 - 5.5 Stainless steel spatula or scoop
 - 5.6 Aluminum weighing dishes or porcelain crucibles for percent solids determination
 - 5.7 Desiccator
 - 6.0 REAGENTS
 - 6.1 Distilled or deionized water - ultra pure for preparation of standards and for dilution of samples.
 - 6.2 Phosphoric acid solution, 1:1 by volume.
 - 6.3 Stock Standards
 - 6.3.1 Potassium hydrogen phthalate, stock solution, (10,000 mg carbon/L). Dissolve 2.128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled or deionized water and dilute to 100 ml in a volumetric flask.
 - 6.3.2 Carbonate-bicarbonate, stock solution (5000 mg carbon/L). Dissolve 1.750 g of sodium bicarbonate and 2.209 g of sodium carbonate in distilled or deionized water and dilute to 100 mL in a volumetric flask.
 - 6.4 Working Standards
- All working standards must be prepared fresh daily prior to analysis.

6.4.1 Initial Calibration Standards

Prepare a series of five initial calibration standards, including a blank and four standards, by pipetting appropriate volumes of the stock solution (6.3.1) into separate 50 mL volumetric flasks and diluting to volume. The lowest concentration standard must be prepared to yield an equivalent sample detection limit of 100 mg/Kg on a dry weight basis. The high calibration standard shall define the linear range of the analysis and the remaining standards shall be at graduated intervals between the low and high standards.

6.4.2 Continuing Calibration standard

Prepare a continuing calibration standard from the stock standard solution at a concentration equal to a mid-point standard in the calibration curve.

6.4.3 Initial Calibration Verification Standard

Prepare an initial calibration verification standard at a concentration near the mid-range of the calibration curve, but not equal to the any of the initial calibration standards. The initial calibration verification standard must be prepared from a source other than that used to prepare the initial calibration standards (e.g. second source verification).

6.4.4 Laboratory Fortified Blank

Prepare a Laboratory Fortified Blank (LFB) containing potassium hydrogen phthalate at a concentration equal to the CRQL. One LFB must be prepared and analyzed with each batch of samples prepared and analyzed.

7.0 PROCEDURE

- 7.1 Weigh a portion of well mixed sample (up to 500 mg) into the combustion boat or sample cup. Add 1:1 phosphoric acid drop wise until effervescence stops.
NOTE: The acid must make solid contact with the sample. Heat the sample in a drying oven at 75°C for 1 hour.

NOTE: This procedure will convert inorganic carbonates and bicarbonates to carbon dioxide and eliminate them from the sample.

- 7.2 While the samples are in the oven, establish the appropriate TOC operating conditions and calibrate the analyzer as outlined in Section 8.0.

- 7.3 Analyze the residue according to the instrument manufacturer's instructions.

- 7.4 Determine percent solids on a separate sample aliquot as follows:

- 7.4.1 Record to the nearest 0.01 g the mass of a clean porcelain crucible or aluminum weighing dish.

- 7.4.2 Transfer 5 - 10 g of well mixed soil/sediment into the pre-weighed crucible or weighing dish and record the weight of the sample to the nearest 0.01 g. Dry the sample overnight, or for at least 12 hours, in an oven at 105°C. Allow the sample to cool in a desiccator.

Exhibit D -- Section IV

Part G - Total Organic Carbon in Soil and Sediment

- 7.4.3 Reweigh and record the mass of the oven-dried sample to the nearest 0.01 g. Calculate the Percent Solids content using Equation 1. The total organic carbon concentrations shall be reported relative to the dry weight of soil/sediment/solid.

EQ. 1

$$\% \text{ Solids} = \frac{\text{Sample Dry Wt. (g)}}{\text{Sample Wet Wt. (g)}} \times 100$$

If the soil sample contains a percent solids content of less than or equal to 30% solids, then a larger sample must be analyzed in order to meet the reporting limit requirements.

8.0 CALIBRATION AND ANALYSIS

- 8.1 Allow at least 30 minutes instrument warm-up time. Follow the manufacturer's instructions for assembly/set-up, testing, calibration, and operation.
- 8.3 Calibrate the instrument using the blank and the four calibration standards that cover the analytical range (Section 6.4.1). Prepare a calibration curve plotting mg carbon vs. instrument response. The calibration curve must meet the criteria for linearity specified in Exhibit E, to continue the analysis.
- 8.3.1 If the TOC analyzer prevents the required 5 point calibration, then calibrate according to the instrument manufacturer's recommendations, and analyze the remaining required standards immediately after calibration. The results of all additional standards (except the low standard at the CRQL) shall be within $\pm 20\%$ of the true value. The CRQL standard must be within \pm CRQL value. Each standard's concentration and the calculations to show that the recovery criteria has been met shall be given in the raw data.
- 8.3.2 If the values do not fall within this range, the instrument must be recalibrated and the additional standards reanalyzed. The additional standards must meet the criteria specified in Section 8.3.1 before any samples, QC samples and required blanks are analyzed.
- 8.4 After the instrument has been calibrated, the analytical sequence that is outlined below and described in Exhibit E must be followed. In addition, the quality control criteria specified in Section 10.0 must be adhered to. The results of these analyses must meet the acceptance criteria specified in Exhibit E and Section 10.0 to continue the analysis.
- 8.4.1 Analytical Sequence Summary
- Initial Calibration (blank and 4 standards)
 - ICV, ICB, LFB, carbonate-bicarbonate check standard (see Section 9.2), CCV, CCB
 - 10 analytical samples, maximum (all samples must be analyzed in triplicate and meet the technical acceptance criteria in section 10.3)
 - CCB, CCV (repeated at a minimum every 10 analytical samples, but not to exceed 2 hours)
 - Last analytical sample, carbonate-bicarbonate check standard, LFB, CCV, CCB.
- 8.5 Sample Dilutions
- 8.5.1 Use the results of the original analysis to determine the approximate dilution factor required to bring the response within the initial calibration range.
- 8.5.2 The dilution factor chosen should keep the response in the upper half of the initial calibration range of the instrument.
- 8.5.3 All soil/sediment dilutions are prepared by mixing an aliquot sample with quartz silica sand.

- 8.5.3.1 Weigh to the nearest 0.01 g a representative aliquot of sample to be diluted. The sample amount must be greater than or equal to 0.5 g. To this add a known amount of silica sand, weighed to the nearest 0.01 g, to bring the total weight (sample plus sand) to the approximate dilution factor required. Divide the total weight by the sample weight to determine the actual dilution factor.
- 8.5.3.2 Place the diluted sample in a shaker mill and agitate for 1 minute. If the sample is not uniform in color after the initial agitation period, then continue the agitation in 1 minute intervals until a uniform color is obtained.
- If a shaker mill is unavailable, place the diluted sample in a mortar and using the pestle, grind the sample to a uniform color and consistency.
- 8.5.3.3 If this is an intermediate dilution, use it and repeat the above procedure to achieve larger dilution.
- 8.5.3.4 Analyzed the diluted sample in accordance with Section 8.0.

9.0 CALCULATIONS

Determine the concentration of Total Organic Carbon, mg/Kg, for each sample, QC sample, and required blank using Equation 2.

EQ. 2

$$\text{Total Organic Carbon (mg/Kg)} = \frac{(M_c) (Df)}{\left(\frac{(M_s) (D)}{1000} \right)}$$

Where,

M_c = Mass of organic carbon determined from calibration curve, mg
 M_s = Mass of sample, g
 Df = Dilution factor (If no dilution is performed, $Df = 1$)
 $D = \frac{\% \text{ Solids}}{100}$
 1000 in the denominator converts g to Kg

10.0 QUALITY CONTROL

10.1 Blanks

There are three types of blanks required by this method: the initial calibration blank (ICB), continuing calibration blank (CCB), and preparation blank.

The ICB and CCB consist of a volume of distilled or deionized water that is analyzed in the same manner as the analytical standards. The results of the ICB and CCB analyses indicate whether there is contamination in the system from a previous sample.

The preparation blank consists of a few drops of 1:1 phosphoric acid (similar quantity as required for samples analyses) that is placed in the combustion boat or sample cup and carried through the identical analysis procedures as the samples in an SDG. If additional preparation techniques are used, such as sample dilutions with silica sand, a preparation blank must be subjected to the same techniques. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

10.1.1 Frequency

All blanks (ICB, CCB, preparation blank) must be analyzed at the frequency specified in Exhibit E.

10.1.2 Procedure

Prepare and analyze all blanks in accordance with Sections 7.0 and 8.0 and Exhibits E.

10.1.3 Calculations

Determine the total organic carbon content for each blank using Equation 2.

10.1.4 Technical Acceptance Criteria

All blanks must be prepared and analyzed at the frequency described in Section 10.1.1 and must meet the acceptance criteria specified in Exhibit E for blank analyses.

10.1.5 Corrective Action

If the technical acceptance criteria for blank analyses are not met, then the contractor must stop and correct the problem before continuing.

Any blank that fails to meet the technical acceptance criteria as specified in Section 10.1.1 and Exhibit E for blank analyses must be reanalyzed at no additional cost to the Agency. Furthermore, all samples, including the duplicate and matrix spike samples, associated with the blank that does not meet the technical acceptance criteria for blanks must also be reanalyzed at no additional cost to the Agency.

If sample analyses are reported with non-compliant blanks, then the contractor shall receive a commensurate reduction in sample price depending upon the impact of the non-compliance on data usability.

10.2 Carbonate-Bicarbonate Check Standard

The carbonate-bicarbonate check standard analysis provides information regarding the efficiency of the CO₂ removal through acidification and heat.

10.2.1 Frequency

The carbonate-bicarbonate check standard must be analyzed prior to the analysis of any samples, QC samples, or required blanks, and after the last sample in the analytical sequence (refer to analytical sequence summary, Section 8.4.1). The analysis conditions for the carbonate-bicarbonate check standard must be the same as those for the analytical samples.

10.2.2 Procedure

The carbonate-bicarbonate check standard consists of a weighed portion of silica sand (approximately 100 mg) that is placed in the combustion boat or sample cup and spiked with 200 µL of the carbonate-bicarbonate stock solution. The sample is then dried in an oven and taken through the preparation and analysis procedure in Sections 7.0 and 8.0. This check standard is equivalent to approximately 2000 mg/Kg carbonate-bicarbonate. Results of carbonate-bicarbonate check standard analyses shall be reported on FORM 2A.

10.2.3 Calculations

Determine the concentration of any inorganic carbon not removed using Equation 2.

10.2.4 Technical Acceptance Criteria

Carbonate-bicarbonate check standards must be prepared and analyzed at the frequency described in Section 10.2.1.

10.2.4.1 The concentration of inorganic carbon remaining in the sample must be less than the CRQL.

10.2.5 Corrective Action

If the carbonate-bicarbonate check standard analysis does not meet the technical acceptance criteria in Section 10.2.4, the analysis shall be stopped, the problem determined and the carbonate-bicarbonate check standard must be reanalyzed. The carbonate-bicarbonate check standard analysis must meet the technical acceptance prior to the analysis of any samples, QC samples or required blanks for purgeable organic carbon. Furthermore, all samples, QC samples or required blanks analyzed up until the last compliant carbonate-bicarbonate check standard must also be reanalyzed at no additional cost to the Agency.

If sample analyses are reported with non-compliant carbonate-bicarbonate check standards, then the contractor shall receive a commensurate reduction in sample price depending upon the impact of the non-compliance on data usability.

10.3 Triplicate Sample Analysis (D)

The triplicate sample analysis provides information regarding the precision of the preparation and analysis procedures. Triplicate analyses, along with their average, shall be reported on FORM 1B.

10.3.1 Frequency

Each sample in the Sample Delivery Group (SDG) shall be analyzed in triplicate.

10.3.2 Procedure

Follow the procedures as specified in Section 7.0 and 8.0 for the preparation and analysis of the triplicate samples.

10.3.4 Calculations

10.3.4.1 Determine the total organic carbon content in each of the triplicate sample analyses using Equation 2.

Exhibit D -- Section IV
Part G - Total Organic Carbon in Soil and Sediment

- 10.3.4.2 Calculate the Percent Relative Standards Deviation (%RSD) between the triplicate sample analyses using Equation 3 below. Report %RSD results on Form 1B as described in Exhibit E.

EQ. 3

$$\%RSD = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

Where,

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{(n-1)}}$$

X_i = each individual value used to calculate the mean

\bar{X} = the mean of n values

n = the total number of values

10.3.5 Technical Acceptance Criteria

Triplicate samples must be prepared and analyzed at the frequency described in Section 10.3.1.

- 10.3.5.1 If the average sample concentration is greater than or equal to 5x CRQL, then the %RSD for the triplicate sample analyses shall be used as the control limit. The %RSD result must be $\leq 20\%$.
- 10.3.5.2 If the average sample concentration is less than 5x CRQL, then the CRQL must be entered in the "Control Limit" column on Form 1B. The standard deviation calculated in Equation 3 for the triplicate sample analyses result must be \leq CRQL.

10.3.6 Corrective Action

Samples that do not meet the technical acceptance criteria for triplicate analysis shall be reanalyzed in triplicate at no additional cost to the Agency. Report both the original triplicate analysis and the triplicate re-analysis on Form 1B as described in Exhibit B. If a result does not meet the acceptance criteria in Section 10.3.5, flag the result with an "*" on FORM 1B.

- 10.3.6.1 Triplicate samples **must** be prepared and analyzed for every sample in an SDG. If triplicates are not prepared and analyzed for every sample in an SDG, the contractor shall reprepare and reanalyzed those samples not analyzed in triplicate at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample acceptance criteria.
- 10.3.6.2 Sample results reported without triplicate analyses shall be receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data usability.

10.4 Spike Sample Analysis (S)

10.4.1 Summary

In order to evaluate the effects of the sample matrix and to determine the precision of the method used for TOC determination, a sample must be spiked with organic carbon and analyzed in accordance with the method.

10.4.2 Frequency of Spike Analysis

- 10.4.2.1 A spiked sample analysis must be performed for each group of samples of a similar matrix for the following, whichever is most frequent:
- Each SDG (not to exceed 20 field samples), or
 - Each matrix within an SDG, or
 - EPA may require additional MS analyses, upon Regional request, for which the Contractor will be paid.

- 10.4.2.2 As a part of the Agency's QA/QC program, aqueous equipment and/or field blanks may accompany water samples that are delivered to a laboratory for analysis. The Contractor shall not perform the spike analysis on any of the designated field QC samples.
- 10.4.2.3 The Contractor shall not perform the spike analysis on any designated Performance Evaluation samples.
- 10.4.2.4 If the EPA Region designates a sample to be used as a spiked sample, then that sample must be used.
- 10.4.2.5 If the Contractor has a question regarding the frequency, etc., of the spike analysis for a particular SDG, contact the RSCC for clarification.
- 10.4.3 Procedure for Preparing a spiked sample
 - Prepare a spiked sample by adding a known volume of the potassium hydrogen phthalate stock solution (Section 6.3.1) to an aliquot of the sample chosen for spiking. The final concentration of the spiked sample should be at the mid-range concentration of the calibration curve. Process the sample according to Section 7.0 and 8.0.
- 10.4.3.1 Before performing a spike analysis, analyze the sample used for spiking. If the sample analysis required a dilution to bring the sample results within the calibration range, then the spiked sample should be prepared using the same dilution for which the sample results will be reported to the Agency.
- 10.4.4 Calculations for Spiked Sample Analysis
 - 10.4.4.1 Calculate the TOC concentration of the spiked sample using Equation 2.

- 10.4.4.2 Calculate the recovery of the spiked compound using equation 4.

EQ. 4

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spiked sample result

SR = Average Sample result

SA = Spike added

- 10.4.5 Technical Acceptance Criteria for Spike Sample Analysis

- 10.4.5.1 All Spiked samples must be analyzed on a TOC system meeting the initial calibration, initial calibration verification, and continuing calibration technical acceptance criteria defined in Exhibit E.
- 10.4.5.2 The Spiked samples must be analyzed or reanalyzed within the contract required holding time defined in Section 4.0.
- 10.4.5.3 All spiked samples must have an associated preparation blank, and ICB and CCB blanks that meet the blank technical acceptance criteria defined in Exhibit E.
- 10.4.5.4 The technical acceptance criteria for spiked sample recoveries are given in Exhibit E. These limits are advisory and no further action by the laboratory is required. However, frequent failures to meet the limits for recovery warrant investigation by the laboratory, and may result in questions from the Agency.

- 10.4.6 Corrective Action for Spiked Sample Analysis

Any spiked sample that does not meet the technical acceptance criteria for spiked sample analysis must be reanalyzed at no additional cost to the Agency. Both sets of data must be reported on separate Forms 5A and must distinguish between the initial analysis and the reanalysis using the suffixes in Exhibit B.

- 10.4.6.1 Corrective actions for failure to meet initial and continuing calibration and initial calibration verification must be completed before the analysis of any QC samples.
- 10.4.6.2 Corrective actions for failure to meet all blank technical acceptance criteria must be met before the analysis of any QC samples.
- 10.4.6.3 The contractor must make every effort to reanalyze the sample within the contract required holding times.

- 10.5 Laboratory Fortified Blank (LFB)

The Laboratory Fortified Blank (LFB) analysis verifies the accuracy at the Contract Required Quantitation Limit.

10.5.1 Frequency

One LFB must be prepared and analyzed with each batch of samples prepared and analyzed. The LFB must be analyzed after the initial calibration blank, prior to the analysis of any samples, and after the last sample in the analytical sequence (refer to the analytical sequence summary, Section 8.4.1). The preparation and analysis conditions for the LFB must be the same as those for the analytical samples.

10.5.2 Procedure

Prepare an LFB containing potassium hydrogen phthalate at a concentration equal to the CRQL. Process the LFB according to the procedures specified in Section 7.0.

10.5.3 Calculations

Calculate the percent recovery of the LFB using Equation 5:

EQ. 5

$$\text{Percent Recovery (\%R)} = \frac{M}{T} \times 100$$

Where,

M = Measured analyte concentration

T = True analyte concentration.

10.5.4 Technical Acceptance Criteria

The LFB must be prepared and analyzed at the frequency described in Section 10.5.1. The LFB must meet the acceptance criteria specified in Exhibit E for LFB analyses.

10.5.5 Corrective Action

If the LFB does not meet the technical acceptance criteria in Section 10.5.4, then the analysis shall be terminated, the problem corrected and the samples associated with that LFB redigested and reanalyzed. The LFB analysis must meet the technical acceptance prior to the analysis of any samples, QC samples or required blanks. Furthermore, all samples, QC samples or required blanks analyzed up until the last compliant LFB must also be reanalyzed at no additional cost to the Agency.

If sample analyses are reported with non-compliant LFB analyses, then the contractor shall receive a commensurate reduction in sample price depending upon the impact of the non-compliance on data usability.

EXHIBIT D
PART H - TOTAL COMBUSTIBLE ORGANICS (TCO) IN SOILS

ANALYTICAL METHODS

1.0 Scope and Application

The analytical method that follows is designed to measure the amount of organic matter in peats and other organic soils, such as organic clays, silts and mucks. The method includes procedures for moisture removal and sample ashing for a final determination of total combustible organics as a percentage of oven dried mass. This method is based on ASTM D 2974-87, *Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils*, and has been modified for EPA New England.

2.0 Summary of Method

A measured amount of peat or organic soil sample is allowed to air-dry overnight and the percent moisture removed is calculated. A portion of the air-dried sample is then homogenized, dried in an oven at 105°C, and the total moisture content (air-dried plus oven-dried) is determined and expressed as a percentage of the as-received mass. The oven dried sample is then ignited in a muffle furnace at 750°C and the total combustible organics is determined and expressed in mg/Kg of oven-dried mass.

3.0 Apparatus

3.1 Balance - top-loading balance capable of weighing 300 g \pm 0.01 g. The balance must be calibrated in accordance with ASTM E 617 specifications each 8-hour work shift. The balance must also be checked annually by a certified technician. All balance calibration checks and maintenance must be recorded in a bound logbook and a copy of this information must be submitted with the sample data package.

3.2 Oven - capable of being regulated to a constant temperature of 105 \pm 5°C. The 105°C oven temperature must be checked daily, prior to use, using a second source thermometer. The second source thermometer temperature must agree within \pm 2°C of the oven thermometer or digital readout. If this limit is not met, then the problem thermometer must be determined and replaced, or if the oven uses a digital readout, the digital readout must be recalibrated or a compliant thermometer must be used in its place. All thermometers must be checked at least annually against a primary reference thermometer. All thermometer checks must be recorded in a bound logbook and a copy of this information must be submitted with the sample data package.

3.3 Muffle Furnace - capable of producing a constant temperature of 750°C \pm 15°C. The 750°C furnace temperature must be checked daily, prior to analysis, using a second source thermometer or thermocouple. The temperatures must agree within \pm 15°C for the analysis to continue. If this criteria is not met, the thermometer or thermocouple which is out of calibration must be determined and replaced. All thermometer or thermocouple calibration checks must be recorded in a bound logbook and a copy of this information must be submitted with the sample data package. (NOTE: Following the temperature check, reduce the furnace temperature to less than 200°C in preparation for analysis.)

3.5 Evaporating Dishes or crucibles - made of high silica or porcelain of not less than 100 mL capacity.

3.6 Aluminum Foil - heavy duty

Exhibit D -- Section IV
Part H - Total Combustible Organics

- 3.7 Porcelain Pan, Spoons, and equipment of the like.
- 3.8 Desiccator
- 4.0 Procedure
- 4.1 Moisture Content
 - 4.1.1 Air-Dried Moisture
 - 4.1.1.1 Place a representative field sample on a square rubber sheet, oil cloth, or equivalent material. Mix the sample thoroughly, remove any sticks and large stones that are not consistent with the sample make-up, and, if necessary, reduce the amount of sample by quartering. Work rapidly to prevent moisture loss. If the sample contains excessive water the following steps must be taken:
 - 4.1.1.1.1 If the sample contains standing or free flowing water and is not amenable to the sample preparation discussed in 4.1.1.1, decant any water layer present from the sample container, remove any sticks and large stones that are not consistent with the sample make-up, and proceed to 4.1.1.2. The contractor shall document the problem, and the EPA sample numbers of the affected samples, in the SDG narrative.
 - 4.1.1.2 Record to the nearest 0.01 g the mass of the large flat pans.
 - 4.1.1.3 Transfer 200 to 300 g of representative sample to a pre-weighed pan. Spread the sample out evenly and crush soft lumps with a spoon or spatula.

Note: Two 50 g aliquots of air-dried sample shall be required for the oven-dried moisture determination in Section 4.1.2. Thus, the contractor must adjust the quantity of sample aliquoted for air-drying based on the estimated moisture level present in the original sample.
 - 4.1.1.4 Reweigh the pan and record the mass of the sample, as-received, to the nearest 0.01 g.
 - 4.1.1.5 Let the samples come to moisture equilibrium with room air by allowing the samples to air-dry for a minimum of 24 hours. Stir the sample at least two times, once per 12 hour period, to maintain maximum air exposure of the entire sample. When the mass of the sample reaches a constant value, less than 0.02 g change over a 1 hour period, proceed to 4.1.1.6. Record all sample weights to the nearest 0.01 g in determining the air-dried constant mass.
 - 4.1.1.6 Weigh the pan to the nearest 0.01 g and record the final constant mass of the air-dried sample.
 - 4.1.2 Oven-Dried Moisture
 - 4.1.2.1 The following cleaning procedure must be performed for all high silica or porcelain evaporating dishes used to determine total combustible organics:
 - 4.1.2.1.1 Clean all evaporating dishes with soap and hot water followed by a deionized/distilled water rinse.

Exhibit D -- Section IV
Part H - Total Combustible Organics

- 4.1.2.1.2 Place the dishes in a muffle furnace at 750°C for a minimum of 1 hour. Remove the dishes from the furnace and place them in a desiccator to cool (a minimum of 30 minutes).
- 4.1.2.2 Record to the nearest 0.01 g the mass of the clean evaporating dishes.
- 4.1.2.3 Grind the air-dried sample from Section 4.1.1 for 1-2 minutes in a high speed blender. Next, thoroughly mix the air-dried, ground sample and transfer two 50 g aliquots to separate pre-weighed evaporating dishes. (Note: Cover the remainder of the air-dried sample with aluminum foil, until sample analysis is complete, in case reanalysis is required.)
- 4.1.2.4 Weigh the dishes to the nearest 0.01 g and record the mass of each air-dried sample.
- 4.1.2.5 Prior to placing the samples in the drying oven, check and record the oven temperature. (Note, the oven temperature calibration must be checked in accordance with Section 3.2 prior to analysis.) The temperature must be stable at 105°C ± 2°C. If the oven temperature is not within this limit, then adjust the temperature. The oven temperature must be within the limit and remain stable for 1 hour prior to sample analysis.
- 4.1.2.6 Place the samples in the drying oven for a minimum of 16 hours. Monitor and record the temperature of the drying oven after 1-2 hours and prior to removing the samples from the oven. All temperature readings, along with the time were taken, must be recorded in a bound logbook and a copy of this information must be submitted with the sample data package.
- 4.1.2.7 Remove the dishes from the oven, cool in a desiccator, and determine if the samples have reached constant weight using the following steps:
- 4.1.2.7.1 The amount of time the dishes are allowed to cool in the desiccator before weighing must be consistent for each step in the constant weight determination. A desiccation time between thirty (30) and sixty (60) minutes (but no more) is adequate for uniform cooling. Record both the time the samples were placed in the desiccator and the time weighing commenced to determine the total desiccation time.
- 4.1.2.7.2 Weigh the dishes to the nearest 0.01 g and record the mass of each oven-dried sample.
- 4.1.2.7.3 Place the samples back in the oven at 105°C ± 2°C for a minimum of one hour, and repeat the desiccation and weighing process described above. The desiccation time prior to weighing must be consistent with that determined in Section 4.1.2.7.1 for all samples, QC samples and blanks. If the desiccation time is not within ± 10 minutes of the total desiccation time recorded in Section 4.1.2.7.1, then the samples must be returned to the oven for 1 hour and the desiccation and weighing process repeated.
- 4.1.2.7.4 Record the mass of the oven-dried sample following the second drying period. Constant weight is obtained when there is no change in sample weight (± 0.01 g) between two successive drying periods. Repeat this drying process until constant weight is obtained.
- 4.1.2.8 Record to the nearest 0.01 g the final mass of the oven-dried samples at constant weight.
- 4.2 Total Combustible Organics (Organic Matter Content)
- 4.2.1 Place the oven-dried samples, from Section 4.1.2, in a muffle furnace that is at less than 200°C. (Note, the muffle furnace temperature calibration must be checked in accordance with Section 3.3 prior to analysis.) Gradually increase the temperature in the furnace to 750°C ± 30°C. Care must be taken during this step, particularly with oily samples, to avoid loss of sample from the dish due to splattering and/or possible spontaneous combustion. Once the furnace is up to temperature, monitor and record the time and temperature every 15 minutes for the first hour and each additional hour thereafter. Samples must remain at 750°C ± 30°C for a minimum of 2 hours.

Exhibit D -- Section IV
Part H - Total Combustible Organics

- 4.2.2 Remove the dishes from the oven, cool in a desiccator, and determine the constant weight of the ashed samples as described in Section 4.1.2.7 using the muffle furnace at $750^{\circ}\text{C} \pm 30^{\circ}\text{C}$.
- 4.2.3 Record to the nearest 0.01 g the final mass of the ashed samples at constant weight.

5.0 Data Analysis and Calculations

- 5.1 Calculate the percent moisture removed by air drying using Equation 1.

EQ. 1

$$\text{Air-Dried Moisture Content (\%)} = \frac{(A - B)}{A} \times 100$$

Where,

A = Mass of sample as-received, g
B = Mass of air-dried sample, g

- 5.2 Calculate the total percent moisture (air-dried plus oven-dried) for each sample using Equations 2 and 3 below.

- 5.2.1 Based on the weight of air-dried sample transferred into the evaporating dish and the percent moisture removed through air-drying, calculate the equivalent mass of sample transferred to the evaporating dish on an as-received basis using Equation 2.

EQ. 2

$$\text{Equivalent Sample Mass (g)} = \frac{C}{D}$$

Where,

C = Weight of air-dried sample transferred to dish, g
D = $\frac{(100 - \% \text{ Air-dried moisture})}{100}$

- 5.2.2 Calculate the total percent moisture using Equation 3.

EQ. 3

$$\text{Total Moisture Content (\%)} = \frac{(E - F)}{E} \times 100$$

Where,

E = Equivalent sample mass, g (calculated in Equation 2)
F = Mass of oven-dried sample, g

- 5.3 Calculate the Total Combustible Organics (TCO) removed by ashing using Equation 4. TCO is calculated in mg/Kg as oven-dried mass.

EQ. 4

$$\text{Total Combustible Organics (mg/Kg)} = \frac{(F - G)(1000)}{\left(\frac{F}{1000}\right)}$$

Where,

F = Mass of oven-dried sample, g
G = Mass of ashed sample, g
1000 in the numerator converts g to mg
1000 in the denominator converts g to Kg

6.0 Quality Control

6.1 Preparation Blanks (PB)

Sample analysis and reporting must not proceed until all preparation blank technical acceptance criteria are met. Preparation blanks are required for the air-dried percent moisture, oven-dried percent moisture and total combustible organics determinations.

A preparation blank consists of an empty drying pan for the air-dried percent moisture determination and an empty high silica or porcelain evaporating dish for the oven-dried percent moisture and total combustible organics determinations. The preparations blanks must be carried through the entire analytical procedure along with the samples they are associated with. The preparation blank must be the same type of pan and evaporating dish that is used for sample analyses. The high silica or porcelain evaporating dishes must be cleaned by the same procedure described in Section 4.1.2.1.

6.1.1 Frequency

At least one preparation blank must accompany every SDG or batch of samples, whichever is more frequent, through every step of the analysis, including air-drying, oven drying, ashing, and desiccation and weighing.

- 6.1.1.1 Note, if the size of the oven or muffle furnace limits the number of analytical samples in a batch, then a preparation blank must accompany each batch. (Example: If the muffle furnace can only hold a preparation blank and five samples, and the drying oven can hold over 15 samples, then the muffle furnace becomes the determining factor in a batch's size. Thus, for an SDG containing 12 samples, 3 preparation blanks must be included during the oven drying so that each batch of samples going into the muffle furnace has a separate preparation blank. Note, the air-drying procedure uses a separate preparation blank and the limiting factors described in the example do not apply.)

6.1.2 Procedure

Prepare a sufficient number of preparation blanks along with the number of dishes required for sample analysis. Follow the procedure in Section 4.0, making sure that a preparation blank accompanies each batch of samples

Exhibit D -- Section IV
Part H - Total Combustible Organics

throughout each step of the entire process. Determine and record all preparation blank weights along with the sample batch.

6.1.3 Calculations

6.1.3.1 Calculate the absolute value difference between the initial and final weights of the preparation blanks used in the percent air-dried moisture determination (Section 4.1.1).

6.1.3.1 Calculate the absolute value difference between the initial and final weights of the preparation blanks used in the oven-dried moisture determination (Section 4.1.2).

6.1.3.2 Calculate the absolute value difference between the initial and final weights of the preparation blanks used in the combustible organics determination (Section 4.2).

6.1.4 Technical Acceptance Criteria

All preparation blanks must be prepared and analyzed at the frequency described in Section 6.1.1.

6.1.4.1 The absolute value difference for each preparation blank must be ≤ 0.01 g.

6.1.5 Corrective Action

If the technical acceptance criteria for preparation blank analyses are not met, then the contractor must stop and correct the problem before continuing.

Any preparation blank that fails to meet the technical acceptance criteria for blank analyses must be reanalyzed at no additional cost to the Agency. Furthermore, all samples, including duplicate samples, associated with a preparation blank that does not meet the technical acceptance criteria for blanks must be reanalyzed at no additional cost to the Agency.

If sample analyses are reported with non-compliant blanks, then the contractor shall receive a commensurate reduction in sample price or zero payment depending upon the impact of the non-compliance on data useability.

6.2 Duplicate Sample Analysis (D)

The duplicate sample analysis provides information regarding the precision of the preparation and analysis procedures. All duplicate results shall be reported on FORM I - PART 3 as described in Exhibit B.

6.2.1 Frequency

As described in the procedure in Section 4.0, every sample in the Sample Delivery Group (SDG) shall be analyzed in duplicate for percent moisture and total combustible organics (Sections 4.1.2 and 4.2, respectively). That is to say, from the single air-dried sample (Section 4.1.1) duplicate aliquots are removed and carried through the remainder of the procedure for percent moisture and TCO determinations. In addition, one sample per SDG (not to exceed 20 field samples) must be carried through the entire procedure, including the air-drying step, in duplicate. (Thus, that one sample in the SDG shall contain duplicate air-dried portions, and each of these air-dried portions shall in turn be analyzed in duplicate for percent moisture and TCO.)

6.2.2 Procedure

Prepare each sample following the procedures specified in Section 4.0. Results for duplicate sample analyses shall be reported on FORM IC as described in Exhibit B. Total moisture content shall be reported as a percentage of mass as-received and total combustible organics shall be reported in mg/Kg of oven-dried mass.

6.2.3 Calculations

- 6.2.3.1 Determine the air-dried moisture content in the original and duplicate samples using Equation 1.
- 6.2.3.2 Determine the total moisture content and total combustible organics in each original and duplicate sample using Equations 2 and 3.
- 6.2.3.3 Determine the average of each original and duplicate.
- 6.2.3.4 Calculate the Relative Percent Difference (RPD) between each original and duplicate sample using Equation 5.

EQ. 5

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where,

RPD = Relative Percent Difference
S = Sample result (original), % or mg/Kg
D = Duplicate sample result, % or mg/Kg

6.2.4 Technical Acceptance Criteria

Duplicate samples must be prepared and analyzed at the frequency described in Section 6.2.2.

- 6.2.4.1 The Relative Percent Difference between all duplicate results must be ≤ 20 %.

6.2.5 Corrective Action

Samples that do not meet the technical acceptance criteria for duplicate analysis shall be reanalyzed, once, at no additional cost to the Agency. An original and duplicate of that sample must be reanalyzed. Report all original and duplicate results for both the original analysis and the re-analysis on FORM I - PART 3 as described in Exhibit B. If an RPD result does not meet the acceptance criteria, flag the result with an "*" on FORM I - PART 3.

- 6.2.5.1 Duplicate samples must be prepared and analyzed at the frequency described in Section 6.2.1, and must include the required blanks. If duplicates are not prepared and analyzed at this frequency, the contractor shall re-prepare and reanalyzed those samples not prepared in duplicate, including the original, at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample acceptance criteria.

Exhibit D -- Section IV
Part H - Total Combustible Organics

- 6.2.5.2 Sample results reported without duplicate analyses shall receive a commensurate reduction in sample price depending upon the impact of the non-compliance on data usability.

PART I - GRAIN SIZE DISTRIBUTION (GSD) IN SOILS

1.0 Scope and Application

This analytical method covers the quantitative determination of the distribution of particle sizes in soils. The distribution of particle sizes larger than 75 μ m (retained on the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 μ m is determined by a sedimentation process, using a hydrometer. This method is based on ASTM D 422-63 (Reapproved 1990), *Standard Test Methods for Particle-Size Analysis of Soils*, and has been modified for EPA New England.

2.0 Summary of Method

A soil/sediment sample is air dried and then separated into two fractions using a No. 10 (2.00 mm) sieve. The fraction that remains on the No. 10 sieve is washed with tap water, dried in an oven at 110°C, and mechanically sieved with an array of sieve sizes that separate the sample into the various gravel and coarse sand fractions. The fraction of sample that passes the No. 10 sieve is subjected to a two part process. First, a hydrometer test is performed which defines the fraction of sample that is silt and clay (less than the No. 200 (75 μ m) sieve). Second, the sample from the hydrometer test is transferred to a No. 200 sieve, and washed with tap water to remove all particles less than 75 μ m. The sample remaining on the No. 200 sieve is then dried in an oven at 110°C, and mechanically sieved with an array of sieve sizes that define the medium and fine sands present in the sample.

3.0 Apparatus

- 3.1 Balances - top-loading balance capable of weighing 300 g \pm 0.01 g for weighing the material passing the No. 10 (2.00 mm) sieve and a balance sensitive to 0.1% of the mass of the sample material retained on a No. 10 sieve (refer to Section 5.1.1 for approximate sample weights required). The balances must be calibrated in accordance with ASTM E 617 specifications each 8-hour work shift. The balances must also be checked annually by a certified technician. All balance calibration checks and maintenance must be recorded in a bound logbook and a copy of this information must be submitted with the sample data package.
- 3.2 Stirring Apparatus - Two types of dispersion devices are provided: a high speed mechanical stirrer (Section 3.2.1), and an air dispersion device (Section 3.2.2). Extensive investigations indicate that air-dispersion devices produce a more positive dispersion of plastic soils below the 20 μ m size and appreciable less degradation on all sizes when used with sandy soils. Because of the definite advantages favoring air dispersion, its use is recommended. The results from the two types of devices differ in magnitude, depending upon soil type, leading to marked differences in particle size distribution, especially for sizes finer than 20 μ m. The type of apparatus used must be noted in the SDG narrative.
- 3.2.1 The first apparatus shall consist of a mechanically operated stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10,000 rpm without load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber, as shown in Figure 1. The shaft shall be of such length that the stirring paddle will operate not less than 3/4 in. (19.0 mm) nor more than 1½ in. (38.1 mm) above the bottom of the dispersion cup. A special dispersion cup conforming to either of the designs shown in Figure 2 shall be provided to hold the sample while it is being dispersed.
- 3.2.2 The second apparatus shall consist of an air-jet dispersion cup conforming to the general details shown in Figure 3.
- 3.2.2.1 The amount of air required by an air-jet dispersion cup is of the order of 2 ft³/min; some small air compressors are not capable of supplying sufficient air to operate the cup.
- 3.2.2.2 Another air-type dispersion device known as a dispersion tube, developed by Chu and Davidson at Iowa State College, has been shown to give results equivalent to those secured by the air-jet dispersion cups. When it is used, soaking of the sample can be done in the sedimentation cylinder, thus eliminating the need for transferring the slurry. When

Exhibit D -- Section IV
Part I - Grain Size Distribution

the air-dispersion tube is used, it must be so indicated in the SDG Narrative.

- 3.2.2.3 Water may condense in air lines when not in use. This water must be removed, either by using a water trap on the lines, or by blowing the water out of the line before using any of the air for dispersion purposes.
- 3.3 Hydrometer - ASTM hydrometers, graduated to read in either specific gravity of the suspension or grams per liter of suspension, and conforming to the requirements for hydrometers 151H or 152H in ASTM Specifications E 100. Dimensions of both hydrometers are the same, the scale being the only item of difference. Hydrometer calibration must be checked daily, prior to use, against distilled or deionized water at 20°C (68°F). For hydrometer 151H the reading must be 1.000 ± 0.001 sp. gr. units, or for hydrometer 152H the reading must be 0 ± 1 g/L. Hydrometer readings must agree within the ranges specified, or the problem hydrometer must be replaced. All hydrometer checks must be recorded in a bound logbook.
- 3.4 Sedimentation Cylinder - A glass cylinder essentially 18 in. (457 mm) in height and $2\frac{1}{2}$ in. (63.5 mm) in diameter and marked for a volume of 1000 mL. The inside diameter shall be such that the 1000 mL mark is 36 ± 2 cm from the bottom of the inside.
- 3.5 Thermometer - A thermometer accurate to 0.5°C. The thermometer must be checked daily for accuracy against a primary reference thermometer prior to use. Temperatures must agree within $\pm 0.5^\circ\text{C}$, or the problem thermometer must be determined and replaced. All thermometer checks must be recorded in a bound logbook.
- 3.6 Sieves - A series of sieves, square-mesh woven-wire cloth, that conform to the requirements of ASTM Specifications E 11. The following sieves (at a minimum) must be included in the analysis:
- | | | | | | |
|----|--------------------|-----------|-----|---------|----------------------|
| 1) | 3 in. | (75 mm) | 8) | No. 10 | (2.00 mm) |
| 2) | 2 in. | (50 mm) | 9) | No. 20 | (850 μm) |
| 3) | $1\frac{1}{2}$ in. | (37.5 mm) | 10) | No. 40 | (425 μm) |
| 4) | 1 in. | (25.0 mm) | 11) | No. 70 | (212 μm) |
| 5) | $\frac{3}{4}$ in. | (19.0 mm) | 12) | No. 140 | (106 μm) |
| 6) | $\frac{3}{8}$ in. | (9.5 mm) | 13) | No. 200 | (75 μm) |
| 7) | No. 4 | (4.75 mm) | | | |

- 3.6.1 The EPA may request up to five (5) additional sieves be included in the analysis.
- 3.7 Water Bath or Constant Temperature Room - A water bath or constant-temperature room for maintaining the soil suspension at a constant temperature during the hydrometer analysis. A satisfactory water tank is an insulated tank that maintains the temperature of the suspension at a convenient constant temperature at or near 20°C (68°F). Such a device is illustrated in Figure 4. In cases where the work is performed in a room at an automatically controlled constant temperature, the water bath is not necessary.
- 3.8 Beaker - A beaker at 250 mL capacity.
- 3.9 Timing Device - A watch or clock with a standard second hand.
- 3.10 Mortar and Rubber-Covered Pestle - suitable for breaking up the aggregations of soil particles.
- 3.11 Ro-Tap sieve shaker, or equivalent
- 3.12 Pycnometer - 25 mL capacity
- 4.0 Reagents
- 4.1 Distilled or deionized water - The distilled or deionized water for a hydrometer test shall be brought to the temperature that is expected to prevail during the hydrometer test. For example, if the sedimentation cylinder is to be placed in the water bath, the distilled or deionized water to be used shall be brought to the temperature of the controlled water bath; or, if the sedimentation cylinder is used in a room with controlled temperature, the reagent water for the test shall be at the temperature of the room. The basic temperature for the hydrometer test is 20°C (68°F). Small variations of temperature do not introduce differences that are of practical significance and do not prevent the use of corrections derived as prescribed.
- 4.2 Dispersing Agent

Sodium hexametaphosphate solution (sometimes called sodium metaphosphate): Weigh 40 g of $\text{Na}_6(\text{PO}_3)_6$ into a 1000 mL flask, dissolve, and dilute to 1 liter with distilled or deionized water.
- 4.1.1 Solutions of this salt, if acidic, slowly revert or hydrolyze back to the orthophosphate form with a resultant decrease in dispersive action. Solutions must be prepared just prior to use (not more than one month) or the pH must be adjusted to between 8 and 9 with sodium carbonate. The pH adjusted solutions must be prepared at least every six months, and the pH must be checked immediately prior to use with wide range pH paper. If the pH of the solution has dropped below 8, a fresh solution must be prepared. The date of preparation and, if applicable, the pH of the solution must be recorded on the solution container and in a bound logbook. A copy of this information must be submitted with the raw data.
- 5.0 Procedure
- 5.1 Test Sample Preparation
- 5.1.1 Decant any standing water and remove any sticks, leaves, or foreign objects that may be present in the sample. Next, expose the entire soil sample to the air at room temperature. Spread the sample out evenly in a pan and crush soft lumps with a spoon or spatula. Let the samples come to moisture equilibrium with room air by allowing the samples to air-dry for a minimum of 24 hours. Stir the sample twice per 12 hour period to maintain maximum air exposure of the entire sample.
- 5.1.2 Once the sample is thoroughly air-dried, break up any aggregations present in a mortar with the rubber-covered pestle. Homogenize the sample and select a representative aliquot for analysis by quartering. The mass of air-dried soil selected for purpose of testing shall be sufficient to yield quantities for mechanical analysis as follows:
- 5.1.2.1 In the preparation procedure that follows, the sample is divided into two portions that are analyzed separately. One portion contains only particles retained on a No. 10 (2.00) sieve while the other portion contains only particles passing the No. 10 sieve. The size of the

Exhibit D -- Section IV
Part I - Grain Size Distribution

sample chosen for analysis shall depend on the maximum particle size retained on the No. 10 sieve, according to the following:

Nominal Diameter of Largest Particles in. (mm)	Approximate Minimum Mass of Portion, g
3/8 (9.5)	500
3/4 (19.0)	1000
1 (25.4)	2000
1½ (38.1)	3000
2 (50.8)	4000
3 (76.2)	5000

- 5.1.2.2 For the portion of the sample passing the No. 10 sieve, the minimum sample size required for analysis shall be approximately 115 g for sandy soils and approximately 65 g for silt and clay soils.
- 5.1.3 Based on the sample size requirements in Section 5.1.2, select an appropriate portion of air-dried sample for purpose of testing and record the mass as the mass of the total test sample uncorrected for hygroscopic moisture.
- 5.1.4 Separate the test sample into two portions by sieving with a No. 10 (2.00 mm) sieve. Grind that fraction retained on the No. 10 sieve in a mortar with the rubber-covered pestle until the aggregations of soil particles are broken up into the separate grains. Place the ground soil back in the No. 10 sieve and again separate into the two fractions. Repeat this process, if necessary, to break up all remaining sample aggregations.
- 5.1.5 After the final sieving, wash the sample fraction retained on the No. 10 sieve free of all fine material with tap water and transfer to a clean, pre-weighed, sample dish. Dry the sample to constant mass in a drying oven at $110 \pm 5^{\circ}\text{C}$ ($230 \pm 9^{\circ}\text{F}$), cool in a desiccator, and weigh. Record the mass of sample retained on the No. 10 sieve as the mass of coarse material.

5.1.5.1 To determine constant mass, after the initial weighing, place the sample back in the oven at $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for a minimum of one hour and repeat the desiccation and weighing process. Constant weight is obtained when there is no change in sample weight (less than $\pm 0.1\%$ change in weight) between two successive drying periods. Repeat this drying process until constant weight is obtained.

5.1.6 From these two masses, the percentages retained and passing the No. 10 sieve can be calculated in accordance with Section 6.1.1.

5.1.6.1 At this point the contractor must perform a check on the mass values obtained (and the thoroughness with which sample clods were pulverized) by weighing the portion passing the No. 10 sieve and adding this value to the mass of the washed and oven-dried portion retained on the No. 10 sieve. Calculate the percent of sample lost by washing using Equation 1.

EQ.1

$$\text{Mass removed by washing (\%)} = \frac{A - (B + C)}{A} \times 100$$

Where,

A = Mass of original air-dried sample

B = Mass of oven-dried sample retained on the No. 10 sieve

C = Mass of air-dried sample passing the No. 10 sieve

5.1.6.2 If the amount of sample lost due to washing is greater than 2%, the sample must be reprepared. If there is insufficient sample to re-perform the preparation, the Contractor shall contact the RSCC for instructions. The Region shall either require that the sample not be analyzed, or shall require that a reduced amount sample be used for the preparation, or shall require the Contractor to continue with the sample analysis. The Contractor shall document the problem, the EPA sample numbers for the affected samples (including the percent of sample lost from washing), and the Region's instructions in the SDG Narrative.

5.2 Sieve Analysis of Portion Retained on No. 10 (2.00 mm) Sieve

5.2.1 Separate the oven-dried portion retained on the No. 10 (2.00 mm) sieve into a series of fractions using the 3 in. (75 mm), 2 in. (50 mm), $1\frac{1}{2}$ in. (37.5 mm), 1 in. (25.0 mm), $\frac{3}{4}$ in. (19.0 mm), $\frac{3}{8}$ in. (9.5 mm), No. 4 (4.75 mm), and No. 10 (2.00 mm) sieves. Additional sieves may be requested by the EPA depending on the sample or upon the specifications for the material under test.

5.2.2 Conduct the sieving operation using a mechanical sieve shaker that simulates a lateral and vertical motion of the sieve, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments in the sample through the sieve by hand. Continue sieving until not more than 1 mass % of the residue on a sieve passes that sieve during 1 minute of sieving.

5.2.3 Determine the mass of each fraction on a balance conforming to the requirements of Section 3.1. At the end of weighing, the sum of the masses retained on all the sieves used must equal closely the original mass of the quantity sieved.

Exhibit D -- Section IV
Part I - Grain Size Distribution

- 5.2.3.1 Calculate the percent recovery of sample after sieving by dividing the sum total of the individual sieve fractions by the original mass of oven-dried sample retained on the No. 10 sieve and multiplying by 100. The percent recovery must be between 99-100%, inclusive, to continue the analysis. If the percent recovery is outside this control limit, then the analysis must be stopped, the problem corrected, and a fresh aliquot of air-dried sample must be reanalyzed, at no additional cost to the Agency, beginning with Section 5.1.4.

If sample analyses are reported with a non-compliant sieving recovery, then the contractor may receive a commensurate reduction in sample price depending upon the impact of the non-compliance on data usability.

5.3 Hydrometer and Sieve Analysis of Portion Passing the No. 10 (2.00 mm) Sieve

5.3.1 Determination of Composite Correction for Hydrometer Reading

- 5.3.1.1 Equations for percentages of soil remaining in suspension, as given in 6.3.3, are based on the use of distilled or deionized water at 20°C (68°F). To compensate for the experimental variations described below, a composite correction must be applied to each hydrometer reading.
- 5.3.1.1.1 A dispersing agent is used in the water which results in a specific gravity of the liquid that is appreciably greater than that of distilled or deionized water.
- 5.3.1.1.2 Both soil hydrometers are calibrated at 20°C (68°F), and variations in temperature from this standard temperature produce inaccuracies in the actual hydrometer readings. The amount of the inaccuracy increases as the variation from the standard temperature increases.
- 5.3.1.1.3 Hydrometers are graduated by the manufacturer to be read at the bottom of the meniscus formed by the liquid on the stem. Since it is not possible to secure readings of soil suspensions at the bottom of the meniscus, readings must be taken at the top and a correction applied.
- 5.3.1.1.4 The net amount of the corrections for the three items enumerated is designated as the composite correction, and must be determined experimentally.
- 5.3.1.2 Measurement of the composite corrections shall be made at two temperatures spanning the range of expected test temperatures, and corrections for the intermediate temperatures calculated assuming a straight-line relationship between the two observed values. For convenience, a graph or table of composite corrections for a series of 1° temperature differences for the range of expected test temperatures may be prepared and used as needed.
- 5.3.1.2.1 Place 125 mL of dispersing agent (4.2) in a sedimentation cylinder and dilute to 1000 mL with distilled or deionized water. Place the sedimentation cylinder in the water bath, or constant-temperature room, set for one of the two temperatures to be used. When the temperature of the liquid becomes constant, insert the hydrometer, and, after a short interval to permit the hydrometer to come to the temperature of the liquid, read the hydrometer at the top of the meniscus formed on the stem. For hydrometer 151H the composite correction is the difference between this reading and one; for hydrometer 152H it is the difference between the reading and zero. Bring the liquid and the hydrometer to the other temperature to be used, and secure the composite correction as before.
- 5.3.1.2.2 The Contractor must submit the composite correction analysis data, along with the raw data from the hydrometer analyses, with the sample data package.

5.3.2 Hygroscopic Moisture Determination

When the sample is weighed for the hydrometer test, weigh an auxiliary portion of between 10 to 15 g sample into a preweighed porcelain evaporating dish. Record the sample weight to the nearest 0.01 g. Dry the sample to constant mass in an oven at $110 \pm 5^\circ\text{C}$ ($230 \pm 9^\circ\text{F}$) for a minimum of 4 hours, cool in a desiccator, and reweigh (refer to Section 5.1.5.1). All sample weights must be recorded in a bound logbook and a copy of this information must be submitted with the sample data package.

5.3.3 Soil Specific Gravity Determination

Use the following method to determine the specific gravity of the soil used in the hydrometer test.

- 5.3.3.1 Weigh a clean dry 25 mL pycnometer to the nearest 0.01 g. Fill the pycnometer with distilled or deionized water, insert the thermometer, and dry off the outside of the flask. Adjust the temperature of the pycnometer to 20°C and tip-off any excess water that exits the side tube. Recap the side tube and reweigh the pycnometer to the nearest 0.01 g. Determine the total volume, in milliliters, of water that is contained in the pycnometer at 20°C using Equation 2.

EQ. 2

$$\text{Pycnometer Volume (mL)} = \frac{W}{D}$$

Where,

W = Weight of water in filled pycnometer (g)
D = Density of water at 20°C (0.9982 g/mL)

- 5.3.3.2 Place 10 to 15 g of oven-dried sample into a pre-weighed pycnometer of known volume (Section 5.3.3.1) and determine the weight of the sample to the nearest 0.01 g. Fill the remaining volume of the pycnometer with deionized or distilled water, insert the thermometer and dry the outside of the flask. Adjust the temperature of the pycnometer to 20°C and tip-off any excess water that exits the side tube. Recap the side tube and reweigh the pycnometer to the nearest 0.01 g to determine the weight of water added. From this, determine the volume of the water added to the pycnometer by dividing the weight of water added by the density of water at 20°C (i.e., 0.9982 g/mL).
- 5.3.3.3 Determine the volume, in milliliters, that the sample occupies in the pycnometer by subtracting the volume of water added (Section 5.3.3.2) from the total volume of the pycnometer (determined in Section 5.3.3.1). From this, determine the equivalent mass of water that this volume represents by multiplying the volume occupied by the soil (mL) by the density of water at 20°C (0.9982 g/mL).

Exhibit D -- Section IV
Part I - Grain Size Distribution

- 5.3.3.4 Calculate the specific gravity of the sample by dividing the mass of the sample by the mass of the equal volume of water that the sample occupies (determined in Section 5.3.3.3). The specific gravity of the sample, including all raw data from the determination, must be recorded in a bound logbook and a copy of this information must be submitted with the sample data package
- 5.3.4 Dispersion of Soil Sample
- 5.3.4.1 Weigh out a portion of air-dried sample, from that passing the No. 10 sieve, for the hydrometer analysis. When the soil is mostly of the clay and silt sizes, weigh out a sample of air-dry soil of approximately 50 g. When the soil is mostly sand the sample should be approximately 100 g.
- 5.3.4.2 Place the sample in the 250 mL beaker and cover with 125 mL of sodium hexametaphosphate solution (40 g/L). Stir until the soil is thoroughly wetted. Allow to soak for at least 16 hours.
- 5.3.4.3 At the end of the soaking period, disperse the sample further, using either stirring apparatus described in Section 3.2.
- 5.3.4.3.1 If the mechanical stirring apparatus (Section 3.2.1) is used, transfer the soil/water slurry from the beaker into the special dispersion cup shown in Figure 2, washing any residue from the beaker into the cup with distilled or deionized water. Add distilled or deionized water, if necessary, so that the cup is more than half full. Stir for a period of 1 minute.
- 5.3.4.3.2 If the air dispersion stirring apparatus (3.2.2) is used, remove the cover/cap and connect the cup to a compressed air supply by means of a rubber hose. An air gauge must be on the line between the cup and the control valve. Open the control valve so that the gauge indicates 1 psi (7 kPa) pressure. Transfer the soil/water slurry from the beaker to the air-jet dispersion cup by washing with distilled or deionized water. Add distilled or deionized water, if necessary, so that the total volume in the cup is 250 mL, but no more. (The initial air pressure of 1 psi is required to prevent the soil/water mixture from entering the air-jet chamber when the mixture is transferred to the dispersion cup.)
- Place the cover/cap on the cup and open the air control valve until the gauge pressure is 20 psi (140 kPa). Disperse the soil for 15 minutes. Soils containing large percentages of mica need be dispersed for only 1 minute.
- After the dispersion period, reduce the gauge pressure to 1 psi preparatory to transfer of soil/water slurry to the sedimentation cylinder.
- 5.3.5 Hydrometer Test
- 5.3.5.1 Immediately after dispersion, transfer the soil/water slurry to the glass sedimentation cylinder, and add distilled or deionized water until the total volume is 1000 mL.
- 5.3.5.2 Using the palm of the hand over the open end of the cylinder (or rubber stopper in the open end), turn the cylinder upside down and back for a period of 1 minute to complete the agitation of the slurry.

- 5.3.5.2.1 The number of turns during this minute should be approximately 60, counting the turn upside down and back as two turns. Any soil remaining in the bottom of the cylinder during the first few turns should be loosened by vigorous shaking of the cylinder while it is in the inverted position.
- 5.3.5.3 At the end of 1 minute, set the cylinder in a convenient location and take hydrometer readings at the following intervals of time (measured from the beginning of sedimentation): 2, 5, 15, 30, 60, 240, and 1440 minutes. If the controlled water bath is used, the sedimentation cylinder should be placed in the bath between the 2 and 5 minute readings.
- 5.3.5.4 When it is desired to take a hydrometer reading, carefully insert the hydrometer, about 20 to 25 seconds before the reading is due, to approximately the depth it will have when the reading is taken. As soon as the reading is taken, carefully remove the hydrometer and place it with a spinning motion in a sedimentation cylinder containing clean distilled or deionized water.
- 5.3.5.4.1 It is important to remove the hydrometer immediately after each reading. Readings shall be taken at the top of the meniscus formed by the suspension around the stem, since it is not possible to secure readings at the bottom of the meniscus.
- 5.3.5.4.2 Clean the hydrometer between readings with a clean soft cloth. If an oily residue appears on the hydrometer, the hydrometer must be cleaned with a soft cloth wet with methanol or isopropanol and then rinsed with distilled or deionized water.
- 5.3.5.5 After each reading, record the time that the reading was taken and the temperature of the suspension (to the nearest 1°C) by inserting the thermometer into the suspension.
- 5.3.5.6 Determine the corrected hydrometer reading by subtracting the composite correction factor, for the temperature at which the reading was taken (Section 5.3.1), from the actual recorded reading (Section 5.3.5.4). All hydrometer readings and corrected hydrometer readings, including the time and temperature at which they were taken, must be recorded in a bound logbook and a copy of this information must be submitted with the sample data package
- 5.3.6 Sieve Analysis on Portion Passing the No. 10 (2.00 mm) Sieve
- After taking the final hydrometer reading, quantitatively transfer the contents of the sedimentation cylinder to a No. 200 (75 µm) sieve and wash the sample with tap water until the wash water is clear. Transfer the material on the No. 200 sieve to a suitable container and dry to constant weight in an oven at $110 \pm 5^{\circ}\text{C}$ ($230 \pm 9^{\circ}\text{F}$) (refer to Section 5.1.5.1 for constant weight determination). Perform a sieve analysis of the portion retained using the No. 20 (850 µm), No. 40 (425 µm), No. 70 (212 µm), No. 140 (106 µm), and No. 200 (75 µm) sieves. Additional sieves may be requested by the EPA depending on the sample or upon the specifications for the material under test.
- 5.3.6.1 Conduct the sieving operation using the mechanical sieve shaker. In no case turn or manipulate fragments in the sample through the sieve by hand. Continue sieving until not more than 1 mass % of the residue on a sieve passes that sieve during 1 minute of sieving.

Exhibit D -- Section IV
Part I - Grain Size Distribution

- 5.3.6.2 Determine the mass of each fraction on a balance conforming to the requirements of Section 3.1. At the end of weighing, the sum of the masses retained on all the sieves used must equal closely the original mass of the quantity sieved.
- 5.3.6.3 Calculate the percent recovery of sample after sieving by dividing the sum total of the individual sieve fractions by the original mass of oven-dried sample retained on the No. 200 sieve and multiplying by 100. The percent recovery must be between 99-100%, inclusive, to continue the analysis. If the percent recovery is outside this control limit, then the analysis must be stopped, the problem corrected, and a fresh aliquot of air-dried sample that passes the No. 10 sieve must be reanalyzed (sieve analysis only, Section 5.3.6), at no additional cost to the Agency.

If sample analyses are reported with a non-compliant sieving recovery, then the contractor may receive a commensurate reduction in sample price depending upon the impact of the non-compliance on data usability.

6.0 Calculations

6.1 Sieve Analysis Values for the Portion Coarser than the No. 10 (2.00) Sieve

- 6.1.1 Calculate the percentage passing the No. 10 sieve by dividing the mass passing the No. 10 by the mass of soil originally split on the No. 10 sieve, and multiplying the result by 100. To obtain the mass passing the No. 10 sieve, subtract the mass retained on the No. 10 sieve from the original mass.
- 6.1.2 To obtain the total mass of soil passing the No. 4 (4.75 mm) sieve, add to the mass of the material passing the No. 10 sieve the mass of the fraction passing the No. 4 sieve and retained on the No. 10 sieve. To obtain the total mass of soil passing the 3/8 in. (9.5 mm) sieve, add to the total mass of soil passing the No. 4 sieve, the mass of the fraction passing the 3/8 in. sieve and retained on the No. 4 sieve. For the remaining sieves, continue the calculations in the same manner.
- 6.1.3 To determine the total percentage passing for each sieve, divide the total mass passing (6.1.2) by the total mass of sample and multiply the result by 100.

6.2 Hygroscopic Moisture Correction Factor

Calculate the hygroscopic moisture correction factor using Equation 2.

EQ. 3

$$\frac{\text{Hygroscopic Moisture}}{\text{Correction Factor}} = \frac{\text{Oven-dried Mass (g)}}{\text{Air-dried Mass (g)}}$$

6.3 Percentages of Soil in Suspension

- 6.3.1 Calculate the oven-dry mass of soil used in the hydrometer analysis by multiplying the air-dry mass used in the hydrometer test (Section 5.3.4.1) by the hygroscopic moisture correction factor (6.2).
- 6.3.2 Calculate the mass of a total sample represented by the mass of soil used in the hydrometer test, by dividing the oven-dry mass used (6.3.1) by the percentage passing the No. 10 (2.00 mm) sieve (6.1.1), and multiplying the result by 100. This value is the weight W in the equation for percentage remaining in suspension.
- 6.3.3 The percentage of soil remaining in suspension at the level at which the hydrometer is measuring the density of the suspension may be calculated as follows:

EQ. 4 - For hydrometer 151H

$$P = \left(\frac{100,000}{W} \times \frac{G}{(G - G_1)} \right) (R - G_1)$$

Note: The bracketed portion of Equation 4 for hydrometer 151H is constant for a series of readings and may be calculated first and then multiplied by the portion in the parentheses.

EQ. 5 - For Hydrometer 152H

$$P = \frac{Ra}{W} \times 100$$

Where,

- a = Correction factor to be applied to the reading of hydrometer 152H. (Values shown on the scale are computed using a specific gravity of 2.65. Correction factors are given in Table 1),
- P = Percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension,
- R = Hydrometer reading with composite correction applied (Section 5.3.5.6),
- W = oven-dry mass of soil in a total test sample represented by mass of soil dispersed (see 6.3.2), g,
- G = Specific gravity of soil particles (determined in Section 5.3.3), and
- G¹ = Specific gravity of the liquid in which soil particles are suspended. Use numerical value of one (1) in both instances in the equation. In the first instance any possible variation produces no significant effect, and in the second instance, the composite correction for R is based on a value of one for G¹.

Table 1

Values of Correction Factor, a, for Different
Specific Gravities of Soil Particles*

Specific Gravity	Correction Factor*
2.95	0.94
2.90	0.95
2.85	0.96
2.80	0.97
2.75	0.98
2.70	0.99
2.65	1.00
2.60	1.01
2.55	1.02
2.50	1.03
2.45	1.05

* For use in equation for percentage of soil remaining in suspension when using hydrometer 152H.

6.4 Diameter of Soil Particles

- 6.4.1 The diameter of a particle corresponding to the percentage indicated by a given hydrometer reading shall be calculated according to Stokes' Law, on the basis that a particle of this diameter was at the surface of the suspension at the beginning of sedimentation and had settled to the level at which the hydrometer is measuring the density of the suspension. According to Stokes' law:

EQ. 6

$$D = \sqrt{\left[\frac{30n}{980} (G - G_1) \right] \times \frac{L}{T}}$$

Where,

- D = Diameter of particles, mm
- n = Coefficient of viscosity of the suspending medium (in this case water) in poises (varies with changes in temperature of the suspending medium),
- L = Distance from the surface of the suspension to the level at which the density of the suspension is being measured, cm. (For a given hydrometer and sedimentation cylinder, values vary according to the hydrometer readings. This distance is known as effective depth (Table 2)),
- T = Interval of time from beginning of sedimentation to the taking of the reading, minutes,
- G = Specific gravity of soil particles, and
- G₁ = Specific gravity (relative density) of suspending medium (value may be used as 1.000 for all practical purposes).

6.4.1.1 Since Stokes' law considers the terminal velocity of a single sphere falling in an infinity of liquid, the sizes calculated represent the diameter of spheres that would fall at the same rate as the soil particles.

6.4.2 For convenience in calculations the above equation may be written as follows:

EQ. 4

$$D = K \sqrt{\frac{L}{T}}$$

Where,

K = Constant depending on the temperature of the suspension and the specific gravity of the soil particles. Values of K for a range of temperatures and specific gravities are given in Table 3. The value of K does not change for a series of readings constituting a test, while values of L and T do vary.

Exhibit D -- Section IV
Part I - Grain Size Distribution

Table 2

Values of Effective Depth Based on Hydrometer and
Sedimentation Cylinder of Specified Sizes**

Hydrometer 151H		Hydrometer 152H			
Actual Hydrometer Reading	Effective Depth L, cm	Actual Hydrometer Reading	Effective Depth L, cm	Actual Hydrometer Reading	Effective Depth L, cm
1.000	16.3	0	16.3	31	11.2
1.001	16.0	1	16.1	32	11.1
1.002	15.8	2	16.0	33	10.9
1.003	15.5	3	15.8	34	10.7
1.004	15.2	4	15.6	35	10.6
1.005	15.0	5	15.5	36	10.4
1.006	14.7	6	15.3	37	10.2
1.007	14.4	7	15.2	38	10.1
1.008	14.2	8	15.0	39	9.9
1.009	13.9	9	14.8	40	9.7
1.010	13.7	10	14.7	41	9.6
1.011	13.4	11	14.5	42	9.4
1.012	13.1	12	14.3	43	9.2
1.013	12.9	13	14.2	44	9.1
1.014	12.6	14	14.0	45	8.9
1.015	12.3	15	13.8	46	8.8
1.016	12.1	16	13.7	47	8.6
1.017	11.8	17	13.5	48	8.4
1.018	11.5	18	13.3	49	8.3
1.019	11.3	19	13.2	50	8.1
1.020	11.0	20	13.0	51	7.9
1.021	10.7	21	12.9	52	7.8
1.022	10.5	22	12.7	53	7.6
1.023	10.2	23	12.5	54	7.4
1.024	10.0	24	12.4	55	7.3
1.025	9.7	25	12.2	56	7.1
1.026	9.4	26	12.0	57	7.0
1.027	9.2	27	11.9	58	6.8
1.028	8.9	28	11.7	59	6.6
1.029	8.6	29	11.5	60	6.5
1.030	8.4	30	11.4		
1.031	8.1				
1.032	7.8				
1.033	7.6				
1.034	7.3				
1.035	7.0				
1.036	6.8				
1.037	6.5				
1.038	6.2				

** Values of effective depth are calculated from Equation 5:

EQ. 5

$$L = L_1 + \left(\frac{L_2 - \frac{V_B}{A}}{2} \right)$$

Where,

L = Effective depth, cm
 L_1 = Distance along the stem of the hydrometer from the top of the bulb to the mark for a hydrometer reading, cm
 L_2 = Overall length of the hydrometer bulb, cm,
 V_B = Volume of hydrometer bulb, cm^3 , and
 A = Cross-sectional area of sedimentation cylinder, cm^2

Values used in calculating the values in Table 2 are as follows:

For both hydrometers, 151H and 152H:

L_2 = 14.0 cm

V_B = 67.0 cm^3

A = 27.8 cm^2

For hydrometer 151H

L_1 = 10.5 cm for a reading of 1.000

2.3 cm for a reading of 1.031

For hydrometer 152H

L_1 = 10.5 cm for a reading of 0 g/L

2.3 cm for a reading of 50 g/L

Table 3

Values of K for Use in Equation for Computing
Diameter of Particle in Hydrometer Analysis

Temperature		Specific Gravity of Soil Particles							
°C	2.45	2.50	2.55	2.60	2.65	2.70	2.75	2.80	2.85
16	0.01510	0.01505	0.01481	0.01457	0.01435	0.01414	0.01394	0.01374	0.01356
17	0.01511	0.01486	0.01462	0.01439	0.01417	0.01396	0.01376	0.01356	0.01338
18	0.01492	0.01467	0.01443	0.01421	0.01399	0.01378	0.01359	0.01339	0.01321
19	0.01474	0.01449	0.01425	0.01403	0.01382	0.01361	0.01342	0.01323	0.01305
20	0.01456	0.01431	0.01408	0.01386	0.01365	0.01344	0.01325	0.01307	0.01289
21	0.01438	0.01414	0.01391	0.01369	0.01348	0.01328	0.01309	0.01291	0.01273
22	0.01421	0.01397	0.01374	0.01353	0.01332	0.01312	0.01294	0.01276	0.01258
23	0.01404	0.01381	0.01358	0.01337	0.01317	0.01297	0.01279	0.01261	0.01243
24	0.01388	0.01365	0.01342	0.01321	0.01301	0.01282	0.01264	0.01246	0.01229
25	0.01372	0.01349	0.01327	0.01306	0.01286	0.01267	0.01249	0.01232	0.01215
26	0.01357	0.01334	0.01312	0.01291	0.01272	0.01253	0.01235	0.01218	0.01201
27	0.01342	0.01319	0.01297	0.01277	0.01258	0.01239	0.01221	0.01204	0.01188
28	0.01327	0.01304	0.01283	0.01264	0.01244	0.01225	0.01208	0.01191	0.01175
29	0.01312	0.01290	0.01269	0.01249	0.01230	0.01212	0.01195	0.01178	0.01162
30	0.01298	0.01276	0.01256	0.01236	0.01217	0.01199	0.01182	0.01165	0.01149

Exhibit D -- Section IV
Part I - Grain Size Distribution

6.5 Sieve Analysis Values for Portion Finer than No. 10 (2.00 mm) Sieve

- 6.5.1 Calculation of percentages passing the various sieves used in sieving the portion of the sample from the hydrometer test involves several steps. The first step is to calculate the mass of the fraction that would have been retained of the No. 10 sieve had it not been removed. This mass is equal to the total percentage retained on the No. 10 sieve (100 minus total percentage passing) times the mass of the total sample represented by the mass of soil used (as calculated in 6.3.2), and the result divided by 100.
- 6.5.2 Calculate next the total mass passing the No. 200 sieve. Add together the fractional masses retained on all the sieves, including the No. 10 sieve (determined in Section 6.5.1), and subtract this sum from the mass of the total sample (as calculated in 6.3.2).
- 6.5.3 Calculate next the total masses passing each of the other sieves, in a manner similar to that given in 6.1.2.
- 6.5.4 Calculate last the total percentages passing by dividing the total mass passing (as calculated in 6.5.3) by the total mass of sample (as calculated in 6.3.2), and multiply the result by 100.

6.6 Graph

A graph of the test results (see FORM I - PART 4B, in Exhibit B) shall be made that includes both the sieve and hydrometer results. For the sieve results, plot the diameter of the particles (i.e. the sieve opening in mm) on the logarithmic scale as the abscissa and the percentages passing corresponding to that diameter on the arithmetic scale as the ordinate. For the hydrometer results, plot each reading taken during the hydrometer test. Plot the diameter of the particles on a logarithmic scale as the abscissa (calculated in Section 6.4) and the percentage of soil remaining in suspension, corresponding to that diameter, on the arithmetic scale as the ordinate (calculated in Section 6.3.3). Draw a line between plotted points to show the natural progression between the diameter of soil particles and the percentages passing.

- 6.7 Refer to Exhibit B for additional Grain Size Determination reporting requirements.

7.0 Quality Control

7.1 Duplicate Sample Analysis (D)

The duplicate sample analysis provides information regarding the precision of the preparation and analysis procedures.

7.1.1 Frequency

Duplicate sample analyses must be performed at the following frequency, whichever is greater:

- 1 duplicate per 10 analytical samples of similar matrix,
- Each matrix within an SDG, or
- EPA may require additional duplicate analyses, upon Regional request, for which the Contractor will be paid.

Duplicate analyses are required for both sieve and hydrometer analyses.

7.1.2 Procedure

Follow the procedures specified in Section 5.0 for the preparation and analysis of the duplicate sample.

7.1.4 Calculations

7.1.4.1 Determine the sample results as specified in Section 6.0 for both the sieve and hydrometer analyses.

7.1.4.2 Calculate the Relative Percent Difference (RPD) between each soil fraction, reported on FORM I - PART 4A, in the original and duplicate sample using Equation 3.

EQ. 9

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where,

RPD = Relative Percent Difference
S = Sample result (original), %
D = Duplicate sample result, %

7.1.5 Technical Acceptance Criteria

Duplicate samples must be prepared and analyzed at the frequency described in Section 7.1.1. Report both the original and duplicate results on separate FORMs I - PARTs 4A and 4B, and on FORM VI - PART 2 as described in Exhibit B. The RPD results on FORM VI - PART 2 must meet a technical acceptance criteria of $\leq 20\%$ for all sieve and hydrometer fractions, except for the sieve that retained the largest particle size. For this sieve size there is no required RPD acceptance criteria. Example: If no particles were retained on the 3/4 in. sieve and the 3/8 in. sieve (located directly below in the stack) was the first sieve to retain particles, the RPD acceptance criteria would not apply to this sieve.

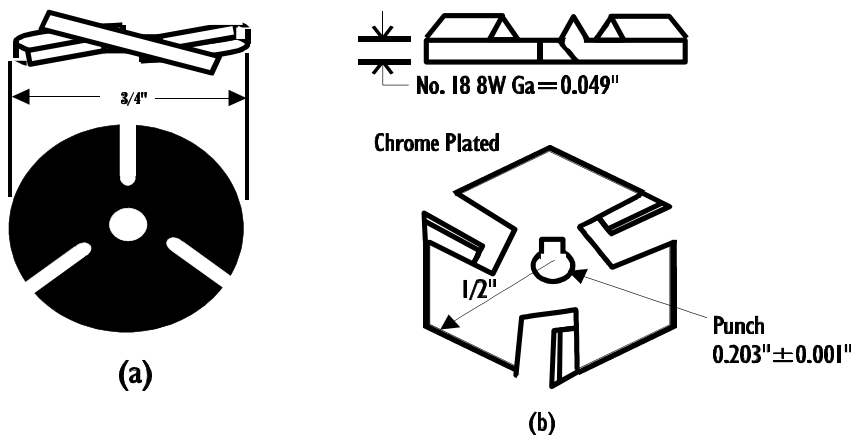
7.1.6 Corrective Action

Samples that do not meet the technical acceptance criteria in Section 7.1.5 for duplicate analyses shall be reanalyzed, once, at no additional cost to the Agency. An original and duplicate of that sample must be reanalyzed. Report both the original and duplicate results for both the original analysis and the re-analysis on FORMs I - PART 4B and FORM VI - PART 2 as described in Exhibit B. If an RPD result does not meet the acceptance criteria, flag the result with an "*" on FORM I - PART 4B and FORM VI - PART 2.

Duplicate samples must be prepared and analyzed at the frequency specified in Section 7.1.1. If duplicates are not prepared and analyzed at this frequency, the contractor shall reprepare and reanalyzed the duplicate sample at no additional cost to the Agency. Reanalyses must be performed within contract required holding times and must meet all sample acceptance criteria.

Sample results reported without duplicate analyses shall receive a commensurate reduction in sample price depending upon the impact of the non-compliance on data usability.

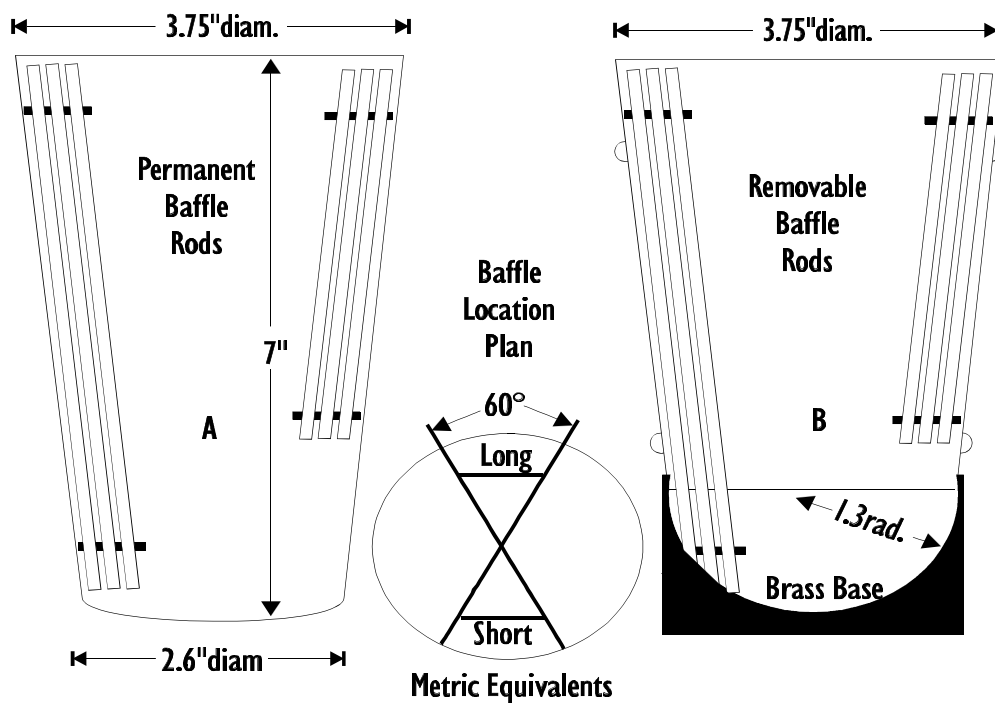
INSERT COREL DRAW FIGURES 1 AND 2



Metric Equivalents

in.	0.001	0.049	0.203	1/2	3/4
mm	003	1.24	5.16	12.7	19.0

FIG. 1 Detail of Stirring Paddles



in.	1.3	2.6	3.75
mm	33	66	95.2

FIG. 2 Dispersion Cups of Apparatus

INSERT COREL DRAW FIGURES 3 AND 4

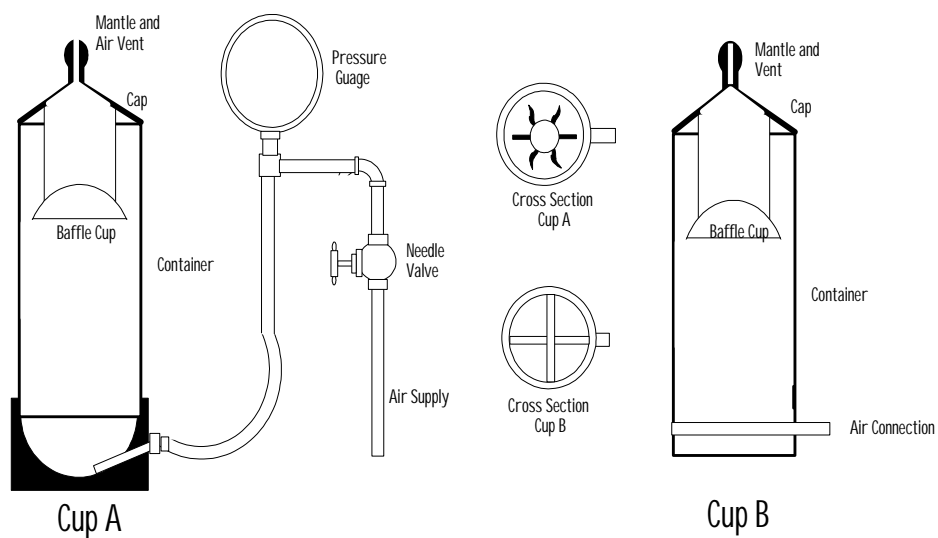
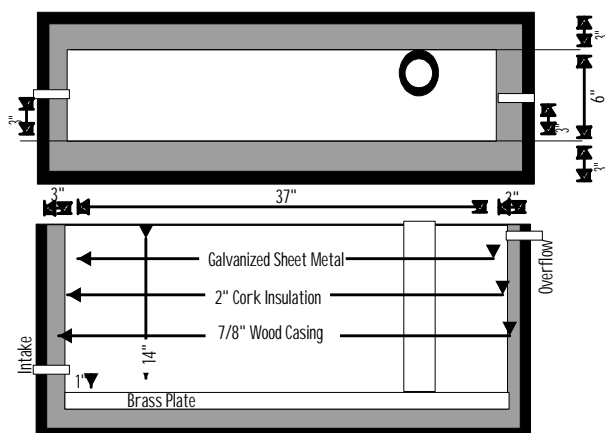


Fig. 3 Air-Jet Dispersion Cups of Apparatus B



Metric Equivalents

in.	7/8	1	3	6 1/4	14	37
mm	22.2	25.4	76.2	158.2	356	940

Fig. 4 Insulated Water Bath